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INORGANIC SEMINARS

1958 - 1959

TABLE OF CONTENTS

1958/1959

CYANOSULFANES - L. C. Thompson	1
FACTORS AFFECTING BOND-STRENGTH OF MOLECULAR ADDITION COMPOUNDS - Ronald O. Ragsdale	5
REACTIONS OF ELEMENTAL SULFUR - N. J. Rose	10
PRINCIPLES AND APPLICATIONS OF RAMAN SPECTROSCOPY - Richard L. Carlin	14
MECHANISM OF OCTAHEDRAL SUBSTITUTION IN METHANOL - Robert E. Sievers	22
UNUSUAL OXIDATION STATES AMONG THE TRANSITION METALS - James E. Huheey	25
RECENT CHEMISTRY OF THE HALOGENS - Darel K. Straub	28
THE HYDRATION OF IONS - A. Wallace Cordes	33
CATALYSIS OF ORGANIC REACTIONS BY METAL CARBONYLS - John G. Verkade	36
THE INFRARED SPECTRA OF SOLIDS - Mitsuru Kubota	39
ELECTRON TRANSFER AND HETEROGENEOUS CATALYSIS - C. H. Travaglini	43
THERMAL DECOMPOSITION OF THE NITROGEN OXIDES - L. C. Thompson	47
ELECTRON DEFICIENT COMPOUNDS - Dean W. Dickerhoof	53
THE LOWER HALIDES OF BORON - James E. Huheey	57
BASICITY OF AMINES - L. J. Sacks	60
AMPHOTERIC AMIDES OF THE TRANSITION METALS - D. K. Straub	65
PREPARATION AND PROPERTIES OF SILYLPHOSPHINE - Donald A. Wenz	69
SOME INORGANIC RING SYSTEMS - Richard L. Carlin	72
SEPARATION OF COORDINATION COMPLEXES BY ADSORPTION METHODS - C. Y. Fujikawa	76
FERRIC PHOSPHATE COMPLEXES - J. S. Oh	79
SOLID ROCKET PROPELLANTS - R. E. Eibeck	82
LIQUID PROPELLANT ROCKETS - N. J. Rose	85
INFRARED SPECTRA OF CHELATED CARBONYL COMPOUNDS - R. E. Sievers	89

L. C. Thompson

September 23, 1958

I. Introduction

Among the compounds containing sulfur and the cyanide group, cyanogen thiocyanate ($S(CN)_2$), thiocyanogen ($(SCN)_2$), sulfur dithiocyanate ($S(SCN)_2$), and disulfur dithiocyanate ($S_2(SCN)_2$) have long been known. The workers who first prepared them regarded these substances either as pure or mixed pseudohalogens (halogenoids) or as thiocyanate derivatives of SCl_2 or S_2Cl_2 . It was only recently, however, that Feher suggested that these compounds be considered as cyano derivatives of the sulfanes, that is, as cyanosulfanes (e.g., $S_2(SCN)_2$ becomes $S_4(CN)_2$ -dicyanotetrasulfane) (1).

II. Preparation of the four previously-known cyanosulfanes

A. Dicyanomonosulfane. This compound has been prepared by the interaction of aqueous KSCN with an ethereal solution of $CNBr$ (2) and by the action of SCl_2 on $Hg(CN)_2$, ICN on $Ag(SCN)$, and S_2Cl_2 on $AgCN$ (3). The last reaction actually gives a mixture of $S(CN)_2$ and $S_3(CN)_2$. $S(CN)_2$ can be obtained as white crystals melting at $62^\circ C$ by the reaction of $S_2(CN)_2$ with $Hg(CN)_2$ (4).

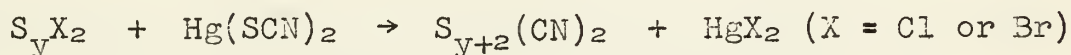
B. Dicyanodisulfane (Thiocyanogen). Early attempts to prepare dicyano disulfane led to the preparation of dicyanomonosulfane and are the present methods of preparing the latter compound. The first successful preparation of $S_2(CN)_2$ was accomplished in 1919 by Söderbäck when he treated an ethereal solution of $AgSCN$ with iodine (4). Later experiments have shown that the reaction between $Hg(SCN)_2$ and Br_2 in ethyl bromide gives better results (1). The free halogenoid is obtained by crystallization at $-70^\circ C$. When prepared in this way it melts at -2 to $-3^\circ C$ to a yellow oil which polymerizes at room temperatures to the insoluble, brick-red parathiocyanogen. Other methods of preparation are to electrolyze alcoholic thiocyanates, to allow MnO_2 to react on $HSCN$ in ether, to treat lead(IV) acetate with $HSCN$ (3) and to treat an acetic acid-acetic anhydride solution of $Pb(SCN)_2$ with Br_2 (5). The analogous behaviour to the halogens is noted by the first two procedures. Thiocyanogen has also been prepared by the interaction of $NOCl$ with potassium thiocyanate in liquid SO_2 at $-30^\circ C$. This product, melting at a much higher temperature ($15-16^\circ C$) than reported above, is claimed to be a more nearly pure substance (6).

C. Dicyanotrisulfane. This was shown to be one of the products of the reaction between S_2Cl_2 and $Hg(CN)_2$ (see above). This compound is also prepared by treating an ethereal solution of $S_2(CN)_2$ with dry H_2S (7) or by the reaction of SCl_2 on an excess of $Hg(SCN)_2$ (1).

D. Dicyanotetrasulfane. $S_4(CN)_2$ can be prepared by the action of S_2Cl_2 on $Hg(SCN)_2$. The compound is isolated at acetone-dry ice temperatures in the form of white crystals. It melts at $-3.3^\circ C$, but is transformed into a glassy mass upon repeated conversion from solid to liquid (8).

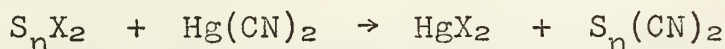
III. Preparation of New Compounds

In 1958 Feher presented the results of his investigation covering not only the preparation of the compounds described above, but also four additional compounds, all of which were now regarded as "cyanosulfanes." The preparation of the cyanosulfane $S_n(CN)_2$ ($n = 1, 2, 3, 4, 5, 6, 7, 8$) was accomplished (with the exception of $S(CN)_2$) using the reaction represented by the equation (1):



It should be noted that earlier worker used the same method to prepare $S_3(CN)_2$ and $S_4(CN)_2$ from the only two dichloro compounds of sulfur known to them.

The determining factor in the reaction appears to be the tendency of sulfur to form chains. This is substantiated by the fact that the reaction represented by the equation:



in which no new sulfur-sulfur bonds are formed, can only be accomplished when $n = 1$ (1).

These higher cyanosulfanes are isolated either as yellow-white solids ($S_5(CN)_2$, $S_6(CN)_2$) or as yellow-green oils ($S_7(CN)_2$, $S_8(CN)_2$) of high viscosity and a large refractive index. They are quite soluble in most organic solvents, but are only slightly soluble in methanol, in which they decompose. Water also decomposes them. As is characteristic of the lower members of the series, the higher cyanosulfanes are polymerized to red, amorphous or glassy, insoluble and infusible products upon heating. However, the higher cyanosulfanes can be kept for weeks at temperatures below $0^\circ C$ without appreciable decomposition (1).

IV. Determination of Structure

The use of physico-chemical properties such as density, refractive index, viscosity and surface tension, which give insights into the constitutions of other series of compounds (e.g., the chlorosulfanes), can not be used in this series since the compounds are not stable (to decomposition or polymerization) under the conditions of the measurements.

A. Raman Spectra (1). The Raman spectra of the cyanosulfanes show four regions to which well-defined vibrations can be assigned.

1. The 2125 cm^{-1} region. The 2125 cm^{-1} region corresponds to the C≡N valence vibration. As in the dinitriles only one C≡N valence vibration is found. Analogously only one S-H valence vibration is to be found in the Raman spectra of the sulfanes.

2. The 670 cm^{-1} region. This region corresponds to the C-S valence vibrations. In organic sulfides ($R-S-R$) and their sulfur analogues ($R-S_n-R$) there are two frequencies around 660 and $630-40\text{ cm}^{-1}$. $n\text{CH}_3\text{SCN}$ also shows two frequencies. In all the cyanosulfanes there is only one frequency.

3. The 440 cm^{-1} region. S-S valence vibrations appear in this region and are known for a large number of compounds (sulfanes, etc.).

4. The 440 cm^{-1} region. Experience with the sulfanes, etc., shows that the deformation frequencies of sulfur chains lie in the 150-250 cm^{-1} region. Consequently all of the bands between 130 and 325 cm^{-1} are assigned to S-S-S or C-S-S bond angle deformations.

B. Crystal Study. A crystal structure study of $\text{S}_3(\text{CN})_2$ has shown that this molecule has an unbranched chain structure with the middle sulfur atom located in a crystallographic mirror plane (9).

Since the same method of preparation is used throughout and since the Raman spectra vary in a consistent manner, it is felt that these compounds may be regarded as members of an homologous series of cyanosulfanes, $\text{NC-S}_n\text{-CN}$.

V. Chemical Properties

No detailed study has been made of the chemical properties of any of these compounds with the exception of dicyanodisulfane (thiocyanogen). Two general properties have been reported, however; namely, that all are hydrolyzed by water and that all members liberate iodine quantitatively from iodides (1).

A. Dicyanodisulfane. This compound has been studied extensively, with respect to its properties as a halogenoid. The organic reactions are summarized by Wood (10).

1. Oxidizing properties. $\text{S}_2(\text{CN})_2$ acts as an oxidizing agent intermediate between bromine and iodine ($E^\circ = -0.77\text{V}$). As such it oxidizes Cu(I) to Cu(II), AsO_3^{-3} to AsO_4^{-3} , H_2S to free S, metals (even as noble as gold) to MeSCN , and $\text{S}_2\text{O}_3^{-2}$ to $\text{S}_4\text{O}_6^{-2}$.

2. Halogenoid properties. Good reviews are given by Walden and Audrieth (3) and by Moeller (11). $\text{S}_2(\text{CN})_2$ forms $(\text{SCN})_3^-$, the interhalogen-halogenoid compounds $(\text{SCNCl})_3$, $(\text{SCNBr})_3$, SCNBr , SCNI , SCNCl_3 , SCNBr_3 , and $\text{I}(\text{SCN})_3$ and the interhalogenoid $\text{NC}\cdot\text{SCN}(\text{S}(\text{CN})_2)$. NOSCN , corresponding to NOCl , is also formed. The compounds of $\text{S}_2(\text{CN})_2$ and chlorine have recently been reinvestigated and it has been shown that monomeric SCNCl can be prepared (12).

3. Other properties. $\text{S}_2(\text{CN})_2$ has been reported to form compounds with the hydrogen halides, such as $(\text{SCN})_2\cdot 2\text{HCl}$ (13). Addition products with BF_3 and BCl_3 have also been reported (14).

B. Dicyanotrisulfane and dicyanotetrasulfane. Solutions of either of these do not react with powdered iron to give thiocyanate unless water is present. This distinguishes them from $\text{S}_2(\text{CN})_2$. However, liquid $\text{S}_4(\text{CN})_2$ reacts with iron powder without the addition of water and also moderately dissolves sulfur (7).

VI. Hydrolysis

The hydrolysis of the cyanosulfanes has been investigated by

several workers. Early workers represented the hydrolysis of thiocyanogen as that of a halogenoid (3):



However, this does not begin to show the complexity which is now known to characterize this hydrolysis. $\text{S}^=$, $\text{S}_2\text{O}_3^=$, $\text{S}_4\text{O}_6^=$, $\text{CO}_3^=$ and NH_3 have also been found among the hydrolysis products (14). The hydrolysis of $\text{S}_3(\text{CN})_2$ and $\text{S}_4(\text{CN})_2$ has been investigated but the data were interpreted as showing that the compounds were the thiocyanate derivatives of $\text{S}(\text{OH})_2$ and $\text{S}_2(\text{OH})_2$, rather than the thiocyanate derivatives of the sulfanes, H_2S and H_2S_2 as had previously been proposed (15).

All the postulations that had been presented prior to Feher's work required the formulation of "fancy" reactions to account for the formation of $\text{CO}_3^=$ and NH_3 . Feher, however, has now proposed that the hydrolysis of the cyanosulfanes be considered as involving the hydrolysis of the $\text{C}\equiv\text{N}$ group first to the amide ($-\text{CONH}_2$), then hydrolysis to the acid and finally decarboxylation of the acid leaving behind the sulfane (16). This explains the formation of both $\text{CO}_3^=$ and NH_3 very nicely. It should be remarked, however, that the hydrolysis of the cyanosulfanes has not been thoroughly investigated and that the work that has been done has been concerned mainly with $\text{S}_2(\text{CN})_2$.

Even in the case of this seemingly simple compound it is readily apparent from the large number of ionic species identified in the hydrolysate, that the course of the reaction is very complex and that no simple equation can be presented for the hydrolytic process.

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FACTORS AFFECTING BOND-STRENGTH OF MOLECULAR ADDITION COMPOUNDS

Ronald O. Ragsdale

September 30, 1958

I. Introduction

According to the Lewis concept, bases, electron pair donors, react with acids, electron pair acceptors to form addition compounds. The synthesis of a large number of molecular addition compounds of the Group III elements has been reported in the chemical literature. Recently enough information has been obtained to make possible a comparison of the relative acidity and basicity of the Lewis acids and bases comprising these addition compounds. The strength of these interactions can be evaluated by investigating the variation in the strength of the coordinate bond that is formed. The strength of the coordinate bond is defined as the enthalpy change, ΔH , accompanying the gas-phase dissociation of the complex (1). It is necessary to work in the gas phase in order to eliminate the heat of sublimation and vaporization of solids and liquids.

II. Methods of Investigating Acid-Base Interactions

The most valuable information can be obtained by investigating the degree of dissociation of the complex in the gas phase. A knowledge of how the degree of dissociation varies with temperature permits the calculation of the thermodynamic functions, ΔH , ΔF , and ΔS . Thus, a quantitative measure of the strength of the coordinate bond can be obtained (2, 3).

The gas-phase dissociation technique is limited because it can not be used on compounds which are easily or difficultly dissociated. A greater range may be obtained by the use of calorimeters and suitable solvents (4).

The relative bond energies have also been established by displacement reactions. This method gives only qualitative results because a displacement reaction depends on differences in free energy between products and reactants and both entropy and solvation effects conceivably determine the results.

Saturation pressures (e.g., vapor pressure of liquid or solid compounds) have been used to give qualitative indication of dative bond strength.

III. Compounds Formed by Group III Acceptor Molecules and Ligands of Group V Atoms

A. Compounds of Boron

The following relative order of stability has been found for compounds of boron with trimethylamine (5): $(CH_3)_3N:BF_3 >$

$(\text{CH}_3)_3\text{N}:\text{BF}_2\text{CH}_3 > (\text{CH}_3)_3\text{N}:\text{BF}(\text{CH}_3)_2 > (\text{CH}_3)_3\text{N}:\text{B}(\text{CH}_3)_3$ (Table, Series 1). Since fluorine is more electronegative than a methyl group, the acidity of BF_3 would be greater than that of $\text{B}(\text{CH}_3)_3$ and the above trend can be easily understood.

The coordinate-bond strength is also affected by the nature of the groups on the donor atom. (Table, Series 2).

The bond strengths of the boron trifluoride adducts of the trimethyl derivatives of Group V elements decrease in the order $\text{N} > \text{P} > \text{As} > \text{Sb}$. (Table, Series 3). Borane, however, shows an order of coordination with the trimethyl derivations of: $\text{P} > \text{N} \gg \text{As} > \text{Sb}$ (6). The order $\text{P} > \text{N}$ is based on a displacement reaction.

Using boron reference acids with small steric requirements, it has been shown (7) that trimethylamine is a better base than ammonia and that trimethylphosphine is a better base than phosphine (8).

The coordinate-bond strength is not always that to be expected from predictions based on Paulings (9) electronegativity values. Using pyridine and nitrobenzene as reference bases, it has been shown (10) that the acceptor power of the boron halides follows the order: $\text{BF}_3 > \text{BCl}_3 > \text{BBr}_3$. The fact that $\text{H}_3\text{As}:\text{BCl}_3$ (11) and $\text{H}_3\text{As}:\text{BBr}_3$ (12) are known, whereas $\text{H}_3\text{As}:\text{BF}_3$ does not form even below -100°C . (13) is another less rigorous example.

B. Compounds of Aluminum

In general the stability of addition compounds formed between ligands of Group V elements and aluminum acceptor molecules is so great that the complexes cannot be studied in the gas phase. The order of coordination $(\text{CH}_3)_3\text{N} > (\text{CH}_3)_3\text{P}$ was established by the displacement reaction (1):



C. Compounds of Gallium, Indium and Thallium

The bond strengths of the addition compounds of trimethyl-gallium and-indium decrease in the order: $\text{N} > \text{P} > \text{As} > \text{Sb}$. (Table, Series 4 and 5). The corresponding $\text{Tl}(\text{CH}_3)_3$ compounds can not be studied in the gas phase because of their instability.

The relative coordinate-bonds strength in the trimethylamine addition compounds of Group III elements decrease in the order $\text{Al} > \text{Ga} > \text{In} > \text{B} > \text{Tl}$ (Table, Series 6). The position of boron in the order of acceptor power is at least partly due to steric factors.

IV. Compounds Formed by Group III Acceptor Molecules and Ligands of Group VI Atoms

A. Compounds of Boron

Bases of Group VI atoms form less stable adducts than do analogous bases of Group V atoms with Group III acceptor molecules (14). The compound $(\text{CH}_3)_2\text{O}:\text{B}(\text{CH}_3)_3$ does not even exist at -78.5°C ., but the compound $(\text{CH}_3)_2\text{S}:\text{B}(\text{CH}_3)_3$ is known (15). With BF_3 the order of coordination is $(\text{CH}_3)_2\text{O} > (\text{CH}_3)_2\text{S} > (\text{CH}_3)_2\text{Se}$ (Table, Series 7). However, with borane, an acid with steric requirements even lower than those of BF_3 , the order of coordination reverts to $\text{S} > \text{O}$ (Table, Series 8).

The etherates of boron trifluoride (Table, Series 9) show the importance of steric effects. Tetrahydrofuran-boron trifluoride is considerably more stable than $(\text{C}_2\text{H}_5)_2\text{O}:\text{BF}_3$.

B. Compounds of Aluminum

Etherates of aluminum trialkyls are so stable that it is not possible to prepare organo-aluminum compounds by the Grignard reaction. The relative bond strengths follow the series $\text{O} > \text{S} > \text{Se} > \text{Te}$ (Table, Series 10).

C. Compounds of Gallium, Indium, and Thallium

For the compounds formed by trimethyl-gallium the order of coordination is $\text{O} > \text{Se} > \text{S} = \text{Te}$ (Table, Series 11) (16). The sequence of coordination is unusual because dimethylselenide forms a less dissociated compound with trimethyl-gallium than does dimethyl sulfide. The addition compounds formed between Group VI ligands and trimethyl-indium or trimethyl-thallium are much less stable than their gallium analogs (1). $(\text{CH}_3)_2\text{O}:\text{In}(\text{CH}_3)_3$ and $(\text{CH}_3)_2\text{S}:\text{In}(\text{CH}_3)_3$ are almost completely dissociated in the vapor phase. Of the Group VI compounds of trimethyl-thallium, only $(\text{CH}_3)_2\text{S}:\text{Tl}(\text{CH}_3)_3$ has a sharp melting point.

GAS-PHASE DISSOCIATION DATA FOR MOLECULAR ADDITION COMPOUNDS
OF GROUP III ELEMENTS (1)

Series	Compound	ΔH kcal/mole	Series	Compound	ΔH kcal/mole
1	$(CH_3)_3N:BF_3$	a	6	$(CH_3)_3N:B(CH_3)_3$	17.62
	$(CH_3)_3N:BF_2CH_3$	23.1		$(CH_3)_3N:Al(CH_3)_3$	a
	$(CH_3)_3N:BF(CH_3)_2$	18.3		$(CH_3)_3N:Ga(CH_3)_3$	21.0
	$(CH_3)_3N:B(CH_3)_3$	17.62		$(CH_3)_3N:In(CH_3)_3$	19.9
				$(CH_3)_3N:Tl(CH_3)_3$	-
2	$H_3N:B(CH_3)_3$	13.75	7	$(CH_3)_2O:BF_3$	13.3
	$CH_3NH_2:B(CH_3)_3$	17.64		$(CH_3)_2S:BF_3$	c
	$(CH_3)_2NH:B(CH_3)_3$	19.26		$(CH_3)_2Se:BF_3$	-
	$(CH_3)_3N:B(CH_3)_3$	17.62			
3	$(CH_3)_3N:BF_3$	a	8	$(CH_3)_2O:BH_3$	-
	$(CH_3)_3P:BF_3$	18.9		$(CH_3)_2S:BH_3$	5.2
	$(CH_3)_3As:BF_3$	-		$(CH_3)_2Se:BH_3$	-
	$(CH_3)_3Sb:BF_3$	b			
4	$(CH_3)_3N:Ga(CH_3)_3$	21	9	$(CH_3)_2O:BF_3$	13.3
	$(CH_3)_3P:Ga(CH_3)_3$	18		$(C_2H_5)_2O:BF_3$	10.9
	$(CH_3)_3As:Ga(CH_3)_3$	10		$(1-C_3H_7)_2O:BF_3$	-
	$(CH_3)_3Sb:Ga(CH_3)_3$	-		$(CH_2)_4O:BF_3$	13.4
5	$(CH_3)_3N:In(CH_3)_3$	19.9	10	$(CH_3)_2O:Al(CH_3)_3$	a
	$(CH_3)_3P:In(CH_3)_3$	17.1		$(CH_3)_2S:Al(CH_3)_3$	8.5
	$(CH_3)_3As:In(CH_3)_3$	c		$(CH_3)_2Se:Al(CH_3)_3$	6
				$(CH_3)_2Te:Al(CH_3)_3$	c
			11	$(CH_3)_2O:Ga(CH_3)_3$	9.5
				$(CH_3)_2S:Ga(CH_3)_3$	--8
				$(CH_3)_2Se:Ga(CH_3)_3$	10
				$(CH_3)_2Te:Ga(CH_3)_3$	--8

Too stable to permit study in the gas phase

Not formed even at $-78^\circ C$.

Too highly dissociated to be measured

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Reactions of Elemental Sulfur

N. J. Rose

October 14, 1958

I. Introduction

In rhombic and monoclinic sulfur the atoms are arranged in puckered octagonal rings (1,2,3,4). Though the structure in the region from the melting point to 160°C has not been clearly characterized, the ring structure apparently exists in liquid sulfur just above the melting point (5,7,8,9). Similarly the sulfur dissolved in inert solvents probably has the S₈ ring structure as is indicated by cryoscopic studies showing sulfur to have a molecular weight corresponding to S₈ (6).

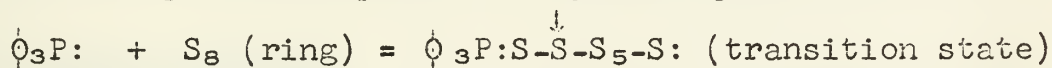
The stoichiometry of reactions involving elemental sulfur (in the ring structure) is often very straight-forward and simple. Until recently, however, the mechanisms by which such reactions take place have been overlooked. The reaction path leading to rupture of the S₈ ring and the subsequent separation of individual sulfur atoms is of special interest.

II. Nucleophilic Displacement

The recent literature contains frequent reference to the rupture of the ring by a nucleophilic displacement of sulfur on sulfur where a Lewis base or an anion is the nucleophile.

A. Triphenylphosphine-sulfur Reaction

On the basis of kinetic studies, Bartlett and Meguerian have proposed that the process represented by the equation



represents the rate determining step in the reaction of O₃P with S₈ in benzene at room temperature (10). In the next step, another O₃P molecule attacks the beta sulfur (marked with arrow) forming O₃PS (sole final product of reaction) and a new polar species with only seven sulfur atoms in the chain. This general process continues until the sulfur chain no longer exists. Eight O₃PS molecules, therefore, result from the rupture of one sulfur ring.

Kinetic studies showed that the reaction is first order with respect to each reactant. This finding is consistent with the proposed bi-molecular mechanism for the rate determining step. The rate of the reaction was found to increase as the solvent was changed from hexane, to benzene, to alpha-bromonaphthalene. This general trend would be expected for reactions in which transition states have polar characteristics compared to the reactants. Instead of pure benzene, acetonitrile, methanol and phenol were used with benzene to provide a mixed solvent for the reaction medium. The rates of reaction increased in the order acetonitrile < methanol < phenol. This increase does not parallel the increase in the mean

dielectric constant of the solution but does parallel the relative hydrogen bonding abilities of the added substances. The opportunity for hydrogen bonding to the terminal sulfur atom in the transition state is better than on phosphorus of ϕ_3P . The transition state is therefore favored which fact accounts for an increase in rate. Para-substituents on the phenyl group in the phosphine molecule significantly change the rate in the way expected. The relative order of reaction rates is tri-p-tolylphosphine > triphenylphosphine > tri-p-chlorotriphenylphosphine. Inductive effects account for the relative nucleophilic character of these bases. The relative sensitivity of the reaction to changes in nucleophilic character is indicated by a value of -2.5 for ρ in the Hammett equation compared to a value of one for ρ in the ionization of substituted benzoic acids (20).

According to Bartlett, the special stability of the S_8 ring with respect to other configurations of sulfur atoms quite possibly makes it more resistant to nucleophilic displacement than other forms (12). The steps following the transition state formation may be rapid for this reason. Also the ensuing reactions require no new anion solvation which fact should facilitate rapid reaction in non-polar solvents. Another contributing feature might be the fact that each attack puts the displaced sulfur atom in the highly stable conditions prevailing in ϕ_3PS .

The rate of reaction is very rapid with hexatomic sulfur in benzene or UV irradiated sulfur in benzene (11). The rates could not be measured under the conditions of the primary experiment. Perhaps the stability of the S_8 ring can again be invoked as an explanation.

B. Cyanide-sulfur Reaction

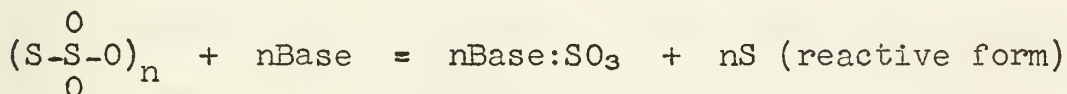
The reaction of CN^- with sulfur in methanol at 40° is mechanistically much the same as the preceding case (13). The product here is exclusively SCN^- (14). Kinetically the reaction was followed at the 260 m μ absorption of sulfur. Here again the reaction was found to be first order with respect to each reactant. The arguments supporting the nucleophilic mechanism are similar to those invoked for the ϕ_3P system. However, water added to the methanol slows down the reaction because of the favored solvation of CN^- with respect to the transition state. Dissolved uni-univalent electrolytes also slow down the reaction.

C. Similar Reactions

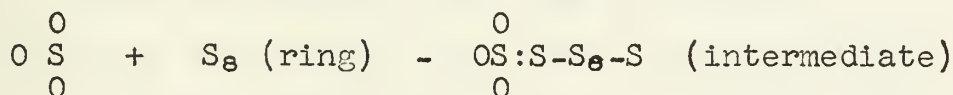
Other reactions whose first step or whole mechanism is similar to ϕ_3P have been proposed. They include the reactions of SO_3^- (15), $(RO_2)OP^-$ (16), P_4 (18), R_3N (19), S^- , SH^- , HSO_3^- and OH^- (17) with sulfur. The reaction of $RC=CR$ with sulfur at $140^\circ C$ is reported to fall into this category (9). However the state of the sulfur at this temperature is presently the subject of rather active controversy and therefore the olefin mechanism seems somewhat speculative.

III. Sulfurtrioxide-sulfur Reaction

Sulfur and liquid SO_3 form the solid polymer $(\text{S}-\overset{\text{O}}{\underset{\text{O}}{\text{S}}}-\text{O})_n$ which is thermally unstable (21). At room temperature the substance decomposes to sulfur and SO_2 . The solvolysis products of $(\text{S}-\overset{\text{O}}{\underset{\text{O}}{\text{S}}}-\text{O})_n$ are neither dithionite nor polythionates but SO_3^- , S_3O_2^- , or SO_4^- . The polymer, as well as SO_3 itself, reacts with dioxane and pyridine. These reactions are represented by the following equation:



When the polymer made by dissolving³⁵ S in SO_3 is itself dissolved in dioxane, no radioactivity is detected in the dioxane- SO_3 addition product (22). On the basis of these experiments it seems that the polymer formula is correct and that the S_8 - SO_3 reaction features the formation of an S-S bond which may have originated by an attack of a sulfur atom in the S_8 ring through the donation of electrons to the sulfur of SO_3 . A possible first step for the reaction is represented by the following equation:



The intermediate may degenerate in the same general way as in the O_3P reaction except that the atoms on the chain are now functioning as electron donors. The $(\text{S}-\overset{\text{O}}{\underset{\text{O}}{\text{S}}}-\text{O})$ units formed in this degeneration

could then polymerize to form the final product. If this speculation is correct, the sulfur ring is a nucleophile in this particular reaction. Conversely the ring is an electrophile in the other reactions mentioned.

IV. Conclusion

In reactions of elemental sulfur, the reaction mechanism must take place initially through the rupture of the S_8 ring. The special significance of this step is clearly demonstrated in the case of the CN^- and O_3P reactions with sulfur.

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Principles and Applications of Raman Spectroscopy

Richard L. Carlin

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Introduction

When visible light passes through a solution, a very small portion of this beam is scattered in different directions. This so-called Rayleigh scattering consists only of the wavelengths of the incident light--there is no change in frequency or wavelength. Raman, however, discovered (1) a series of very weak lines in the scattered radiation whose displacement from the primary line was characteristic of the molecular species present. Thus, for each molecule a similar pattern of lines, the Raman spectrum, is always found, no matter what the incident frequency. It is for this reason that Raman scattering is of interest to the chemist.

Experimental Techniques

In practice, visible or ultraviolet light is produced by a source such as a mercury arc, passed through a filter, and then into the sample bulb. Spectra are then observed in the usual manner at right angles to the incident radiation. It is necessary that the wavelength chosen avoid regions of absorption or photochemical decomposition; this has recently necessitated the use of sources such as the sodium vapor lamp.

The Raman spectra of gases and liquids have been observed, but the largest amount of work has dealt with liquids and solutions. An obvious advantage of this method is that aqueous solutions can be used, since the spectrum of water is much simpler than in the infrared. It is a general rule that Raman spectra are simpler to interpret than infrared spectra, as the former are much less complex. For example, overtones and combination frequencies occur only weakly, if at all.

A principal inconvenience of the method is that all potential light-scatterers, such as traces of dust, fluorescent materials, and the like, must be removed from the sample.

Molecular Light-Scattering

The frequency shifts of the Raman lines relative to the primary line are found to be equal to frequencies of vibrational or rotational transitions of scattering molecules. In Rayleigh scattering the incident light quantum (energy $h\nu^0$) collides with a molecule and is simply scattered without change of frequency. In the Raman effect, the collision induces the molecule to undergo a transition. If, for example, the molecule is in the ground state ($n = 0$) and is excited to the first vibrational state ($n = 1$), corresponding to the frequency V , the light quantum is scattered with correspondingly diminished energy $h(\nu^0 - V)$. If the transition is to the ground state from the first excited state, then the quantum will be scattered with correspondingly greater energy. The two lines are thus the Stokes and anti-Stokes line for this frequency.

The Raman effect should not be confused with fluorescence, where first absorption and then re-emission of light take place. No absorption takes place here, but only scattering. Similarly, while the Raman method is often complementary to the infrared absorption technique, the two are basically different in their selection rules, and should not be confused.

Some Simple Applications

Since the Raman spectrum is characteristic of each type of molecule, it is evident that qualitative and quantitative analysis are readily performed.

Mixed Halides: The Raman spectrum of a mixture of CCl_4 and CBr_4 , or of SiCl_4 and SiBr_4 , consists of a simple superposition of the two components (2); mixtures of SnCl_4 and SnBr_4 give Raman spectra containing new lines not attributable to either constituent (3). The new lines have been shown to be due to the formation of mixed halides in the labile equilibrium:

$\text{SnCl}_4 + \text{SnBr}_4 \rightleftharpoons \text{SnCl}_4\text{-Br}_n + \text{SnCl}_{4-n}\text{Br}_n$. Germanium provides an interesting case in this respect. No mixed halides are observed for silicon (4) and this reaction is instantaneous for tin, but Delwaulle (3) reports that with a mixture of GeCl_4 and GeBr_4 , there is a slow formation of mixed halides which can be followed by taking successive Raman spectra.

Ionic Equilibria: Undissociated nitric acid has a different spectrum than the nitrate ion, freed on dissociation. By measuring the relative amount of each of these species present as a function of hydrogen-ion concentration (6), it is found that nitric acid is most highly dissociated at 7M. In a similar manner, perchloric acid has been found to be the stronger of the two (7).

Principles of Molecular Light-Scattering (8-10)

The application of an applied electric field E will induce a dipole moment P in a molecule by the relation $P = \alpha E$, where α is the polarizability of the molecule. Both P and E are vectors; for an isotropic molecule, α is a scalar. In general, an induced moment need not be in the direction of the applied field, and α is a tensor. The components of P and E are:

$$\begin{aligned} P_x &= \alpha_{xx} E_x + \alpha_{xy} E_y + \alpha_{xz} E_z \\ P_y &= \alpha_{yx} E_x + \alpha_{yy} E_y + \alpha_{yz} E_z \quad (\alpha_{ij} = \alpha_{ji}) \\ P_z &= \alpha_{zx} E_x + \alpha_{zy} E_y + \alpha_{zz} E_z \end{aligned}$$

Now, α can be represented by the six coefficients of the equation:

$$\alpha_{xx} X^2 + \alpha_{yy} Y^2 + \alpha_{zz} Z^2 + 2\alpha_{xy} XY + 2\alpha_{yz} YZ + 2\alpha_{zx} ZX = 1.$$

This is the equation of an ellipsoid, and we shall identify the polarizability with this ellipsoid.

If the axes of the ellipsoid are rotated such that the above equation reduces to :

$$\alpha_{xx}X^2 + \alpha_{yy}Y^2 + \alpha_{zz}Z^2 = 1,$$

then the α_{ii} are called the principal values of α .

Consider a vibrating molecule in which each atom vibrates about its equilibrium position with the same phase and frequency, each atom reaches its position of maximum displacement at the same time, and each atom passes through its equilibrium position at the same time. This vibrational mode is called a normal mode and its frequency is known as a normal or fundamental frequency. Generally, a molecular vibration is complicated, but it can be shown that any such vibration is the superposition of a small number, of normal vibrations. Each normal vibration has its own frequency; if two or three frequencies are the same, the vibrations are degenerate.

A simple molecule usually possesses some symmetry elements, such as a plane of symmetry or an n-fold rotation axis. For each element, there is a corresponding symmetry operation--e.g., reflection in the plane or rotation on the axis. The point group denotes the total number of symmetry elements of a molecule. For the octahedral case, point group O_h , there are twenty-four such elements, for example.

If a molecule is distorted in a normal vibration, and then a symmetry operation characteristic of the undistorted molecule is performed upon it, three modes are found to be important:

- 1) Symmetric modes, where the distorted configuration after the operation is identical with the starting configuration.
- 2) Antisymmetric modes, where the new distorted configuration is equal in magnitude to but opposite in sign from the original distorted molecule.
- 3) Degenerate modes, where the distorted configuration is now a linear combination of two or three normal modes.

If now, during a vibration, in which the polarizability will change, we expand (Taylor's series) the polarizability about the center we have:

$$\alpha = \alpha_0 + (\partial \alpha / \partial q)_0 q,$$

where the zero subscripts refer to the equilibrium configuration. Then, P takes the form,

$$P = \alpha_0 E + (\partial \alpha / \partial q)_0 q E.$$

Let, now, the incident light vibrate with frequency V^0 . The first term in this expression also vibrates with frequency V^0 -- the source of the Rayleigh scattering.

In the second term, q oscillates as V and E as V^0 . Therefore, the term represents electric moments oscillating with frequencies V^0+V . This is the source of the Raman scattering, the intensity of which is determined principally by $(\partial \alpha / \partial q)_0$. This quantity is also a tensor, and it shall be defined as the derived polarizability tensor, α_0' .

Consider light, now, incident along the y -axis and scattering (Rayleigh) at right angles along the x -axis, with the molecule fixed at the origin. Letting the incident light have components E_x and E_y , each will induce dipole moments P_x , P_y , and P_z of the molecule. Since an oscillating dipole does not radiate in its own axial direction, only P_y and P_z will contribute to the scattering along the x -axis, producing plane-polarized components of intensities I_y and I_z , parallel, respectively, to the Y - and Z -axes. For an isotropic molecule (polarizability ellipsoid a sphere) $i = 0$, and the scattering is completely polarized. For non-isotropic molecules, $i = 0$, and $\beta = i/I$ is called the degree of depolarization.

Since Raman scattering depends on α_0' in the same way that Rayleigh scattering depends on α_0 , β' for a Raman line is determined by the nature of the appropriate derived polarizability tensor.

Now, define:

r = a measure of the overall size of the polarizability ellipsoid.

s = a measure of the non-spherical shape of the ellipsoid.

Then, it can be shown that:

$$\beta = \frac{6s^2}{45r^2 + 7s^2}$$

Since r^2 can never be zero for Rayleigh scattering, β is always less than $6/7$; if $\beta = 0$, the scattering is completely polarized.

Analogously, for Raman scattering,

$$\beta' = \frac{6s'^2}{45r'^2 + 7s'^2}$$

r' and s' may both be zero, though, since α_0' is not an ellipsoid. When both r' and s' vanish, $i = I = 0$, and the Raman line is forbidden.

Therefore, the selection rules for the Raman effect are determined by $\alpha_0' = (\partial \alpha / \partial q)_0$, which is in turn determined by the symmetry of the vibrational modes, which are ultimately determined by the shape of the molecule being considered.

For a particular vibration, antisymmetric with respect to some symmetry operation of the undistorted molecule, the performance of this symmetry operation causes the vibrational coordinate q to become $-q$. Since $r' = 0$ (ellipsoid same size as before) but $s' = 0$, then $\beta = 6/7$ for a Raman line that is not otherwise forbidden. This illustrates the selection rule that all permitted Raman lines of antisymmetric modes are depolarized.

If, however, the size and orientation of the ellipsoid remain unaltered in a vibration of, for example, an antisymmetric mode, then this fundamental is forbidden in the Raman effect. This is part of the general selection rule that all vibrations antisymmetric with respect to a center of symmetry are forbidden in the Raman effect. Furthermore, for a molecule possessing a center of symmetry, no vibration can be permitted in both the Raman and infrared absorption spectra.

All Raman lines of degenerate modes are depolarized. Only modes which are symmetric can have $\beta' < 6/7$; these are usually the most intense lines.

Some Applications

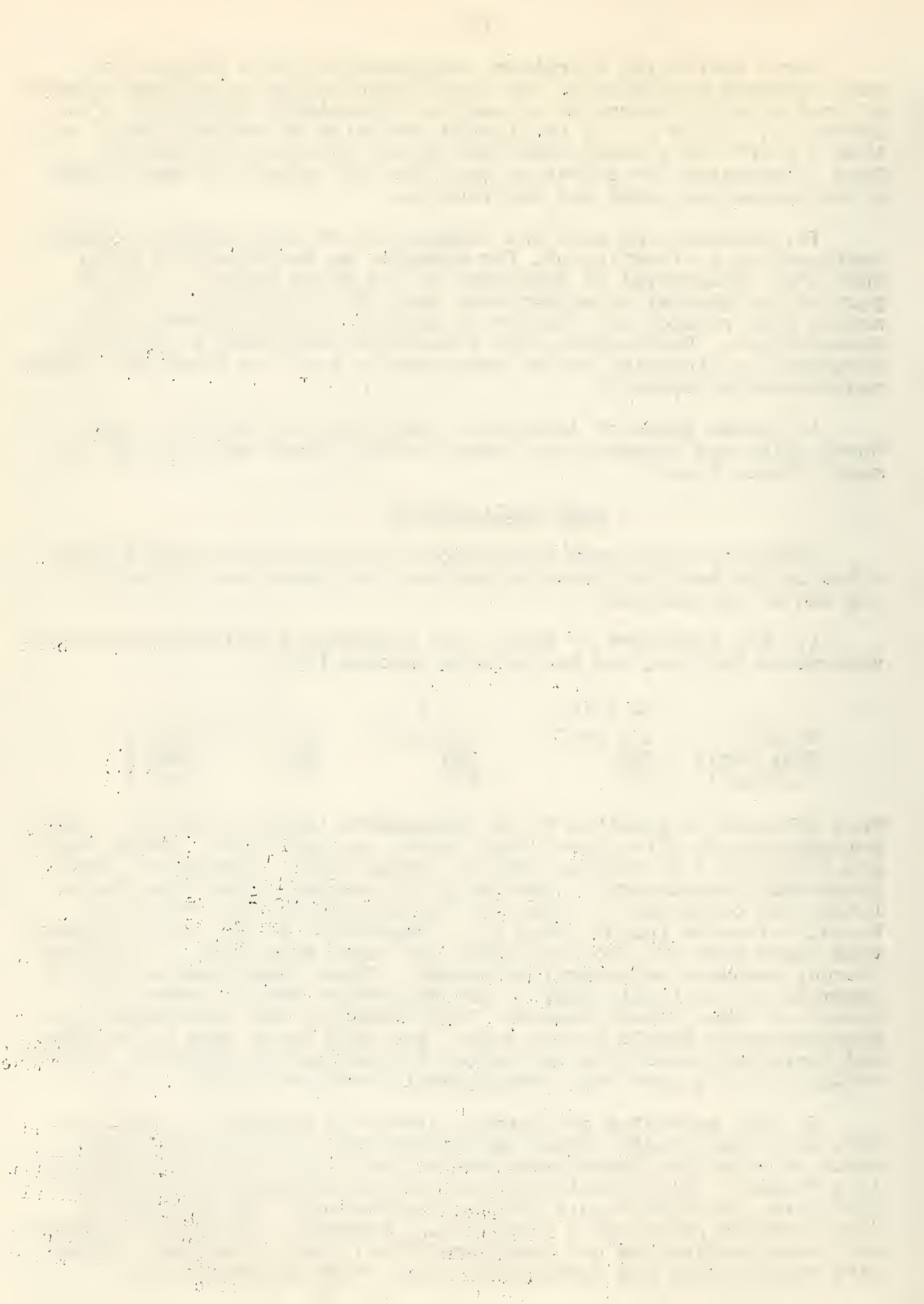
Selection rules have been worked out for various simple molecules on the basis of these principles, and these are tabulated at the end of the abstract.

1. The structure of OsO_4 : The following Raman data have been determined for OsO_4 and two related species (11):

	$V_2 + V_4$	V_3	V_1
$\text{OsO}_4(1)$	335 cm.^{-1}	954 cm.^{-1}	965 cm.^{-1} (pol.)
$\text{ReO}_4^-(\text{aq.})$	332	916	971 (pol.)
$\text{WO}_4^{2-}(\text{aq.})$	324	833	931 (pol.)

This molecule is expected to be tetrahedral (point group T_d). The selection rules allow four Raman lines, one polarized. Three bands are found; $V_2 + V_4$ overlap and are unresolvable. Therefore, OsO_4 is probably tetrahedral. Aqueous ReO_4^- and WO_4^{2-} give three Raman lines, one polarized; these are the selection rules for octahedral molecules (point group O_h). Therefore, it has been proposed that these ions are coordinated to two water molecules in solution, thereby assuming octahedral structure. Since these species should resemble isoelectronic OsO_4 if the structures are the same, the number of Raman lines observed, their position and their degree of depolarization should be the same. The data shows this to be true, and therefore these ions are indeed tetrahedral in solution. These results on OsO_4 have been independently confirmed.(12).

2. XY_3 molecules are usually planar or pyramidal. ClF_3 and BrF_3 have been studied Raman spectroscopically (13) to ascertain which of these two structures obtains, although a third possibility is a T shape. Electron diffraction results indicate the pyramidal structure, but do not rule out the T-structure. The non-zero dipole moment rules out a planar (D_{3h}) symmetry. Previous infrared and Raman studies had not considered the T (C_{2v}) structure. Microwave spectroscopy has demonstrated that these molecules are



T-shaped, and this has now been verified by the Raman method.

3. Woodward and coworkers (14-17) have found that species of the type MX_4^- , where $\text{M} = \text{Ga}, \text{In}$; $\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-$, exist in aqueous solution. If they are tetrahedral, they should have four Raman lines, one polarized. Sample data are:

	V_2	V_4	V_1	V_3
GaBr_4^-	71	102	210(pol.)	278
InBr_4^-	56	79	197(pol.)	238
TlBr_4^-	51	64	190(pol.)	209

These data check with isoelectronic molecules of known tetrahedral structure:

	V_2	V_4	V_1	V_3
SnBr_4	64	88	220(pol.)	279
InBr_4^-	55	79	197(pol.)	239
$\text{CdBr}_4^{=}$	53	62	166(pol.)	183

The gallium dihalides have also been studied (18-19). They have been shown to be tetrahedral in the fused state:

	V_2	V_4	V_1	V_3
$\text{GaCl}_2(\text{fused})$	115	153	346(pol.)	380
$\text{GaCl}_4^- (\text{aq.})$	114	149	346(pol.)	386
$\text{GaBr}_2(\text{fused})$	71	102	210(pol.)	278
$\text{GaBr}_4^- (\text{aq.})$	79	107	209(pol.)	288

This structure persists in the crystalline state (20) and in benzene solution (21).

Selection Rules (22)

<u>Molecule</u>	<u>Example</u>	<u>Point Group</u>	<u>No. of Lines</u>	<u>No. Pol. Lines</u>
AB ₂				
Linear Sym.	CO ₂	D _{∞h}	1	1
Bent Sym.	H ₂ O	C _{2v}	3	2
ABC				
Linear	ClCN	C _{∞v}	3	2
Bent	DOH	C _s	3	3
AB ₃				
Sym. Plane	BF ₃	D _{3h}	3	1
Pyramidal	NF ₃	C _{3v}	4	2
ABO ₂				
Planar Y	COCl ₂	C _{2v}	6	3
Pyramidal	SOCl ₂	C _s	6	4
AB ₄				
Tetrahedral	CH ₄	T _d	4	1
Plane Square	AuCl ₄ ⁻	D _{4h}	3	1
ABO ₃				
3-fold Axis	VOCl ₃	C _{3v}	6	3
Planar	O ₂ NOM	C _s	9	3
AB ₅				
Trigonal Bi-pyramid	PCl ₅	D _{3h}	6	2
Tetragonal pyramid	BrF ₅	C _{4v}	9	3
AB ₆				
Octahedral	SF ₆	O _h	3	1
AB ₈				
Puckered Octagon	S ₈	D _{4d}	7	2
AB ₇				
Pentagonal Bipyramid	IF ₇	D _{5h}	7	2

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-22-

Mechanism of Octahedral Substitution in Methanol

R. E. Sievers

October 28, 1958

I. Introduction

The elucidation of the mechanisms of reactions of octahedral complexes has proven to be a very complex problem. Attempts have been made to categorize these reactions as either S_N1 (substitution, nucleophilic, unimolecular) or S_N2 (substitution, nucleophilic, bimolecular). But in practice an unambiguous determination of the molecularity of such reactions is rarely realized.¹ Bimolecular reactions do not always show second order kinetics.² In the limiting case, S_N1 and S_N2 reaction paths should produce different stereochemical results. However, the stereochemistry of a reaction cannot be predicted without making further assumptions and in practice one is only able to expect that S_N2 reactions would be more stereospecific than S_N1 reactions.³

In predicting whether to expect an S_N1 or S_N2 mechanism, several factors must be considered. These would include the electronic structure of the metal complex, size and charge of the atoms, solvent character and energetic considerations.

Taube,⁴ in his review, used valence bond theory to explain the effect of the electronic structure on the kinetics and mechanisms of reactions. He concluded that the reaction mechanism will depend on the availability of stable inner d orbitals.

Basolo and Pearson³ have applied crystal field theory in their explanation of the kinetic behavior of octahedral complex reactions. They have calculated the energies of activation for the proposed pentacoordinate and heptacoordinate intermediates and conclude that, for Co (III) complexes, the energetically most feasible route is through the S_N1 square pyramid intermediate.

II. Experimental

Most of the mechanistic studies of complexes have been carried out in aqueous solution. Interpretations of the results are complicated by formation of aquo complexes. Direct replacement of one ligand by another is therefore uncommon in water. If a proper solvent were chosen, it might then be possible to avoid the formation of solvated intermediates, and hence to find evidence for a direct bimolecular addition mechanism.

A. Substitution Reactions of $\text{Co(en)}_2\text{Cl}_2^+$ in Methanol.

Brown and Ingold⁵ made a study of the kinetics of substitution of the chloro group in cis- Co(en)_2 by NO_3^- , Cl^- , Br^- , NCS^- , NO_2^- , N_3^- and CH_3O^- . On the basis of this and earlier kinetic and stereochemical studies they advanced a unifying hypothesis which they termed "edge displacement" mechanism.

The reactions were carried out in methanol and were followed by polarimetric, spectroscopic, chemical and radiochemical methods. It was noted that the first four anions (all weakly nucleophilic) react at the same rate and the last three react at greatly

differing rates. Since the first four anions all react at the same rate and furthermore at a rate independent of the concentration of the attacking ion, it was concluded that these displacements proceed by an S_N1 mechanism.

To support this view further, it was observed that the rates of reaction were the same as the rate of racemization of optically active d -cis- $\text{Co(en)}_2\text{Cl}_2^+$.

It was found that for the other three anions (CH_3O^- , N_3^- , and NO_2^-) the second order rates stand in a ratio of 30,000:100:1. While Brown and Ingold interpreted the kinetic results as indicative of a simple S_N2 displacement, Basolo³ pointed out that the methoxide ion data can be interpreted in terms of an S_N1 CB (conjugate base) mechanism with the methoxide ion acting as the conjugate base.

In order to study the effect of a basic anion per se, Basolo and his coworkers⁶ made a study using buffered solutions of trans- $\text{Co(en)}_2\text{Cl}_2^+$ in methanol. They found, for unbuffered solutions, a high rate of chloride release in the case of basic anions such as azide, nitrite and acetate. Buffering the solutions greatly reduced these reaction rates. This supported the belief that conjugate base mechanisms are possible in methanol.

Rate studies were also made on the cis-complex. Buffering, here as before, reduced the rates for basic anions but still the rates are higher than for non-basic anions. Basolo attributes this to ion pair formation. The evidence for ion pair formation is based on a shift in the near ultraviolet spectrum observed for the cis-isomer. This shift does not exist for the trans isomer.

Basolo³ has interpreted the results of these investigations to indicate an S_N1 CB mechanism for methoxide ion and either an S_N1 IP (ion pair) or S_N2 (or S_N2 IP) reaction with other basic anions in the case of the cis complex. For the trans complex in its reaction with weakly basic anions he believes an S_N1 dissociation mechanism to be operative.

B. Substitution Reactions of $\text{Cr}(\text{NH}_3)_2(\text{NCS})_4^-$.

Quite recently, Adamson⁷ has made a kinetic study of the substitution reactions of Reinecke's salt in a number of non-aqueous solvents. He undertook a study of the role of solvent and hydrogen bonding effects on the rates of substitution reactions. A complex was chosen that would be soluble in a variety of non-aqueous solvents and that would be unlikely to become involved in ion-pairing effects.

The rates of solvolysis were determined for $\text{Cr}(\text{NH}_3)_2(\text{NCS})_4^-$ in H_2O , CH_3OH , $\text{C}_6\text{H}_5\text{OH}$, D_2O and nitromethane. For solvents of the ROH type the apparent first order rate constant was 0.01 min.^{-1} at 60° . In D_2O this rate constant was reduced by about 50% and it was very small in the non-hydrogen bonding solvent nitromethane. No evidence for a direct bimolecular substitution was found when anions such as cyanide, azide and iodide were employed in methanol solutions.

Adamson explained the results of the solvolysis reactions in terms of a mechanism designated $\text{S}_\text{N}2$ FS (substitution, nucleophilic, bimolecular: front side attack). This type of mechanism is described as a bimolecular displacement process involving cooperative hydrogen bonding interaction between the anion and the solvent.

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UNUSUAL OXIDATION STATES AMONG THE TRANSITION METALS

James E. Huheey

November 3, 1958

I. Introduction

The subject of unusual oxidation states has attracted considerable attention in recent years. Reviews have been published by Klemm¹, Scholder², and Kleinberg.^{3,4,5,6} It is the purpose of this seminar to summarize briefly some of the methods useful in obtaining transition metals in unusual oxidation states. Since the elements of the first long period are better known than their congeners, they will be discussed more extensively.

Examination of a table of the known oxidation states of the transition metals of the first long period shows an unexpectedly large number of oxidation states. The maximum oxidation state is determined by the number of electrons in the $n s$ and $(n-1)d$ orbitals. For these elements the maximum known oxidation state is equal to the number of unpaired $3d$ electrons plus two. For the elements from Sc to Mn, each additional electron increases the number of electrons which may be either given up entirely or shared with an electronegative element such as fluorine or oxygen. Either type of bonding results in a positive oxidation unit of one per electron. For the elements from Mn to Zn, each additional step across the periodic table removes one d orbital from covalent bonding and increases the effective nuclear charge by one, thus increasing the electronegativity of the metal.

One should expect an oxidation state of plus two for all of the transition metals. This corresponds to the loss of the $4s$ electrons. All of the metals of the first long period do indeed exhibit this state with the exception of Sc, for which only the trivalent state is known.

Concerning the lower oxidation states, several of the metals form carbonyls and cyanide complexes in which the formal oxidation state of the metal is zero or even negative.

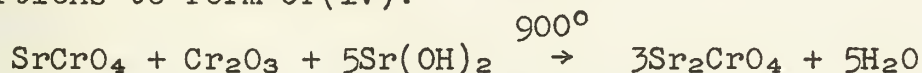
Two limiting factors that often contribute to the instability of a given oxidation state are the oxidizing and reducing properties of water. Thus in 1 M acid solutions a substance with an oxidation potential greater than 0.00 V or a reduction potential greater than 1.23 V is thermodynamically unstable.

II. Preparative Methods

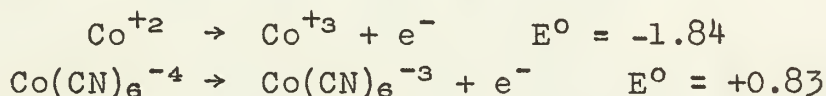
The simplest type of stabilization of unstable oxidation states, but one which is rather fortuitous, is insolubility. Insoluble compounds tend to be stable. Thus MnO_2 is the only simple Mn(IV) compound known. Kleinberg³ has attributed the stability of the hydrazine complex of Cr(II) to insolubility rather than to the reducing properties of hydrazine.

A change of acid concentration may favor one oxidation state over another. Manganate(VI) ion has a reduction potential of $\neq 2.26\text{V}$. However, its oxidation potential is only -0.56 V . Therefore, manganate(VI) can both oxidize water and destroy itself through disproportionation to manganous and permanganate ions. However, if the pH is kept sufficiently high, the manganate(VI) becomes a poorer oxidizing agent and is stabilized.

Scholder⁷ has taken advantage of reversing the tendency towards disproportionation. He calls the phenomenon Symproportionation (Symproportionierung). An example consists of mixing strontium chromate, chromium(III) oxide, and strontium hydroxide in the proper proportions to form Cr(IV):

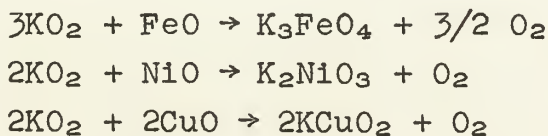


Another method of stabilizing reactive oxidation states is the formation of a complex. In general this stabilizes the desired state by giving a particularly stable hybrid and often making the effective atomic number (e.a.n.) equal to that of the next inert gas. A well known example is:



It will be seen that the limiting factor for the lower oxidation states is the oxidizing property of the hydrogen ion. If we reduce the $[\text{H}^+]$, according to the Nernst equation, we should favor the stability of a reducing agent. If we choose a more basic solvent, qualitatively we should achieve the same effect. Or, to look at it from another point of view, according to the Usanovich concept, an acid and an oxidizing agent are identical; so a more basic solvent such as liquid ammonia should favor the formation of low oxidation states. This is indeed the case, for solutions of alkali metals have been used to reduce metals to the lower oxidation states. Examples are the preparation of zero-valent nickel⁸, zero-valent palladium⁹, zero-valent platinum¹⁰ and a cyanide containing both Mn(0) and Mn(I).¹¹

If the compound we are attempting to prepare is a strong oxidizing agent, a fused salt system is useful. The higher oxides of the transition metals are acid anhydrides and are favored by basic conditions; so fused systems containing an excess of an alkali metal oxide may be used. Klemm postulates that the oxide is converted by an atmosphere of oxygen to the superoxide which in turn oxidizes the metal.^{1,12}



Another method of limited application entails the thermal decomposition of extremely high oxidation states to yield somewhat lower ones. Scholder^{2,7} has prepared Cr(IV), Cr(V), and Fe(IV) by

decomposition of barium chromates and ferrate, respectively. This method is also useful in obtaining the divalent lanthanons.

The last method to be discussed is of both theoretical and practical interest. Selwood¹³ found that decomposition of low concentrations of manganous nitrate on γ -alumina led to the formation of the isomorphous manganese(III) oxide. However, if manganous nitrate is decomposed on a rutile surface, MnO_2 is formed. Similarly, nickel(III) oxide forms on alumina, but nickel(II) oxide forms on magnesia. Jezowska-Trzebiatowska¹⁴ has found that the arsenate ion favors the formation of the manganate(V) ion.

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Recent Chemistry of the Halogens

Darel K. Straub

November 11, 1958

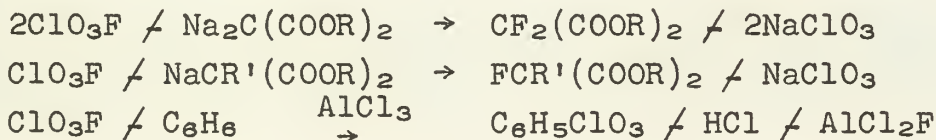
I. Introduction

Modern work on halogen chemistry has been undertaken largely by Schmeisser and co-workers in Germany; Engelbrecht and Cady have also contributed to this field. These investigators have prepared and characterized a variety of unusual oxygen-containing compounds of the halogens. Attention recently has also been directed to the reactions and properties of iodine pentafluoride.

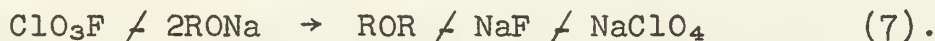
II. Fluorine Derivatives of the Halogen Oxy-Acids

a. Chloryl fluoride. Chloryl fluoride, ClO_2F , was first prepared by Schmitz and Schumacher by fractional distillation of the reaction products of gaseous fluorine on ClO_2 in quartz vessels (1). The possibility of violent explosions renders the procedure dangerous. Introduction of BF_3 into the reaction flask stabilizes the reaction, probably due to the formation of $\text{ClO}_2[\text{BF}_4]$ (2). For the preparation of larger amounts of pure ClO_2F , Schmeisser and Ebenhöch passed fluorine into a concentrated solution of ClO_2 in CCl_3F at -78° (2). Chloryl fluoride is a colorless gas that is very sensitive to moisture. It slowly attacks glass at room temperature and reacts with BF_3 , PF_5 , AsF_5 , and SbF_5 to give white compounds having the compositions $\text{ClO}_2[\text{BF}_4]$, $\text{ClO}_2[\text{PF}_6]$ (m.p. -35°), $\text{ClO}_2[\text{AsF}_6]$ (m.p. 50°), and $\text{ClO}_2[\text{SbF}_6]$ (m.p. 78°), and with SO_3 to give bright orange $\text{ClO}_2[\text{SO}_3\text{F}]$ (2,3).

b. Perchloryl fluoride, ClO_3F . This substance is one of a number of products obtained by the reaction of gaseous fluorine on solid KClO_3 at temperatures less than -20° (4,6). It can be produced in larger quantities by the electrolysis of an ice-cooled, 10% solution of NaClO_3 in anhydrous HF with a potential of 4-7 volts (5). Perchloryl fluoride is a colorless gas, which hydrolyzes only slowly in alkaline solution, in strong contrast to most of the other acyl fluorides. It is thermally stable up to 500° , supports combustion, and has a characteristically sweet odor. By reaction with ammonia, the salt $\text{NH}_4(\text{ClO}_3\text{NH})$ is obtained; organic compounds can be fluorinated or perchlorated:



Sodium alkoxides yield ethers:



c. Chloryl oxyfluoride, ClO_2OF . Bode and Klesper in 1951 isolated from the mixture of products resulting from the reaction of gaseous fluorine on solid KClO_3 at -40° or lower, a colorless gas having the composition ClO_3F (8). Upon hydrolysis, the substance yields fluoride and chloride ions and oxygen, in contrast to perchloryl fluoride which yields fluoride and perchlorate ions. Thus, chloryl oxyfluoride is an isomer of perchloryl fluoride. However, the ClO_2OF

produced is contaminated with large amounts of chlorine and even after fifteen fractional distillations, Engelbrecht could not obtain a pure product (9). The purification is particularly dangerous, since violent explosions occur easily. When Bode and Klesper repeated their experiment, they evidently obtained perchloryl fluoride instead of chloryl oxyfluoride. So far, ClO_2OF has not been obtained pure, and its identity has not been firmly established.

d. Perchloryl oxyfluoride, ClO_3OF . Gaseous fluorine bubbled through 60% perchloric acid in a quartz apparatus yields ClO_4F , along with SiF_4 , O_2 , and OF_2 (10). Rohrbach and Cady could not obtain the compound when an all-carbon apparatus was used. Purification by fractional distillation is hazardous. Perchloryl fluoride is a colorless gas, which has a sharp acid-like odor and explodes upon freezing or contact with grease, water, rubber tubing, or a flame.

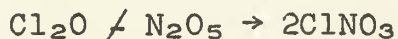
e. Bromyl fluoride, BrO_2F . Schmeisser and Pammer in 1955 prepared BrO_2F by a method analogous to that used for ClO_2F (11). Fluorine was slowly passed into a suspension of BrO_2 in perfluoropentane at -50° , and the light yellow solid which precipitated was fractionally distilled. Bromyl fluoride can also be prepared by allowing BrO_2 to react with BrF_5 at -60° to -50° (12). Liquid BrO_2F attacks glass rapidly, explodes with water, and decomposes violently at 56° to BrF_3 , Br_2 , and O_2 .

f. Iodyl fluoride, IO_2F . Iodine pentoxide dissolves in boiling IF_5 . Upon cooling, white crystals of IOF_3 (or rather, $\text{IO}_2[\text{IF}_6]$) separate. This compound decomposes at 110° to IO_2F (13). Schmeisser and Lang found that iodyl fluoride also resulted when fluorine was passed into a solution of I_2O_5 in liquid HF (14). Iodyl fluoride is a white crystalline solid that is stable in dry air and non-hygroscopic. It reacts with AsF_5 (in HF) to yield white crystals of $\text{IO}_2[\text{AsF}_6]$, and with SbF_5 to yield $\text{IO}_2[\text{SbF}_6]$.

g. Periodyl fluoride, IO_3F . Periodyl fluoride results when fluorine is passed through a solution of HIO_4 in liquid HF (14). The white crystalline material is much more resistant to hydrolysis than IO_2F and can be kept in glass. It decomposes at 90° - 100° , releasing oxygen.

III. Chlorine Nitrate

If Cl_2O and N_2O_5 are mixed in equimolar ratio at liquid air temperature, and the mixture allowed to stand for some hours at -80° and then warmed to room temperature, "chlorine nitrate" is produced quantitatively (15).



The compound ClNO_3 decomposes when mixed with NO_2 at -5° into N_2O_5 and Cl_2 . This suggests the possibility that it is the nitrate of hypochlorous acid. The substance reacts with TiCl_4 (at -80°), SnCl_4 (-60°), SiCl_4 , and ICl_3 (-30°) to give chlorine and $\text{Ti}(\text{NO}_3)_4$ (white crystals, $\text{Sn}(\text{NO}_3)_4$ (white crystals, sublimable), $\text{Si}(\text{NO}_3)_4$, and $\text{I}(\text{NO}_3)_3$, respectively (16). The compound $\text{I}(\text{NO}_3)_3$ is a yellow powder, which decomposes at 0° . When added to a solution of iodine at temperatures below 0° , $\text{I}(\text{NO}_3)_3$ gives INO_3 . Chlorine nitrate with pyridine yields $\text{Cl py}_2 \text{NO}_3$, m.p. 108° (15).

product is a white solid which is soluble in water and in many organic solvents. It is a weak acid and its sodium salt is soluble in water. The product is a white solid which is soluble in water and in many organic solvents. It is a weak acid and its sodium salt is soluble in water.

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VI. CONCLUSIONS

The product is a white solid which is soluble in water and in many organic solvents. It is a weak acid and its sodium salt is soluble in water. The product is a white solid which is soluble in water and in many organic solvents. It is a weak acid and its sodium salt is soluble in water.

REFERENCES

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IV. Fluorine Derivatives of Non-Halogen Acids

a. "Fluorine fluosulfonate". Fluorine will not react with sulfuric acid, but it does react with sulfamic acid above 200° to give SO_3F_2 (17). This compound can be more easily prepared by the reaction of fluorine with SO_3 . Infra-red and nuclear magnetic resonance studies indicate the structure to be FOSO_2F (18).

Other recently investigated compounds with sulfur and fluorine are SOF_4 and SOF_6 , both produced by the fluorination of thionyl fluoride (19). The structures F_4SO and SF_5OF are assigned on the basis of NMR studies (18).

b. Trifluoroacetyl hypofluorite, F_3CCOOF . Cady and Kellogg obtained the compound F_3CCOOF when they permitted water vapor, fluorine, and F_3CCOOH to react (20). The water seemed to act as a catalyst. The compound decomposes completely within a few hours at room temperature.

V. Reactions with Iodine Pentafluoride

Iodine pentafluoride has attracted some attention recently as a non-aqueous solvent. A few of its properties are listed in the table. There is evidence for neutralization reactions in IF_5 , although no pure products have been obtained (21). Both KF and SbF_5 dissolve to produce conducting solutions, from which KIF_6 and $\text{SbF}_4[\text{IF}_6]$ can be isolated. When these solutions are mixed and the solvent removed, $\text{KSbF}_6 \cdot 0.23\text{IF}_5$ remains. The compound KIF_6 was the first reported well-defined polyhalide containing seven atoms (22). Potassium fluoborate can be prepared by passing BF_3 into a solution of KF in IF_5 (21). Potassium iodate dissolves readily in cold IF_5 , without decomposition, and behaves as a normal salt does in water. It is interesting to note that iodine solutions in IF_5 are chocolate brown in color, indicating extensive solvolysis (23).

Iodine pentafluoride reacts with P_2O_5 , V_2O_5 , Cr_2O_3 , WO_3 , and KMnO_4 to give POF_3 , VOF_3 , CrO_2F_2 , $\text{WO}_3 \cdot 2\text{IF}_5$, and MnO_3F , respectively (23,24). Nitrogen (IV) oxide dissolves readily to give a deep cream-colored, crystalline solid, $\text{IF}_5 \cdot \text{NO}_2$, which sublimes unchanged when gently heated. One of the most interesting reactions is that with mercury. Mercury slowly dissolves in refluxing IF_5 to give a dense, buff-colored solid, $\text{Hg}(\text{IF}_5)_2$, which turns red on exposure to air. It is soluble in alcohol, insoluble in chloroform, and hydrolyzes slowly in water. With NaOH solution, yellow HgO , fluoride ion, and iodate ion are produced (23).

Table 1.

Physical Properties of the Halogen Oxy Compounds

Formula	M.P. °C	P.P. °C	Trouton's constant	Reference
ClO ₂ F	-115	-6	23.2	1
ClO ₃ F	-146	-46.8	20.4	7
ClO ₂ OF	-110	-46	20.2	8
ClO ₃ OF	-167.3*	-15.9**	-	10
BrO ₂ F	-9	dec. 56	-	12
IO ₂ F	-	-	-	14
IO ₃ F	dec. 90-100	-	-	14
NO ₂ OCl	-107	18***	-	15, 25
FOSO ₂ F	-158.5	-31.3	22.15	17
F ₄ SO	-99.6	-49.0	22.7	19
SF ₅ OF	-86.0	-35.1	21.9	19
F ₃ CCOOF	-	-21.5-	-	20

* Calculated From Cooling Curve

** At 755 mm Hg

*** Extrapolated

Table II.

Properties of Iodine Pentafluoride (26,27)

M.P. 9.6°

B.P. 98°

Density at 0° 3.75 g/ml

Dielectric constant at 25° 36

Specific conductance in HF at 25° $1.53 \cdot 10^{-5}$ /ohm cm

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A. Wallace Cordes

November 18, 1958

I. Introduction

It has always been assumed that ions in aqueous solution are hydrated. It is necessary to know the extent of this hydration to fully understand electrolytic solutions. Unfortunately the common use of the hydration concept implies a greater understanding than we now possess. Too often hydration is used as a convenient excuse for anomalies in theories of solutions.

II. Ionic Hydration Theories

Early hydration theories pictured the ions as being chemically bonded to the water molecules of hydration. Then from 1920 to 1940 the success of the Debye-Huckel theory in accounting for properties of dilute electrolyte solutions led to the adoption of a more physical than chemical interpretation of ion-solvent interactions. The energy of this interaction was given in terms of the bulk dielectric constant of the solvent. However, it soon became apparent that the use of the macroscopic dielectric constant could not suffice for all energy calculations in more concentrated solutions, and a molecular approach was necessary. Recognition of this need plus new methods of investigation have revived interest in the hydration of ions.

Most current theories refer to "primary" and "secondary" hydration to differentiate the water molecules directly adjacent to the ion from the bulk of the solvent.¹ Robinson and Stokes² show that only a small polyionic ion is likely to exert appreciable orienting effects on a second sheath of water molecules.

Some theories attempt to account for all of the hydration interaction and its effects by considering only the primary hydration. In such a theory Buckingham³ assumes an immobilized layer of four or eight water molecules surrounding the ion, and calculates the interaction energies of these molecules. The remainder of the solvent is considered as a continuous medium.

One of the more popular models, advocated by H. S. Frank,^{4,5} gives more emphasis to the secondary hydration. Frank proposes a model in which the ion is surrounded by a sheath of comparatively immobilized water molecules. Between this sheath and normally structured water exists a region of "structure-breaking" water. This structure-breaking region is due to a balance between two orienting tendencies: the normal structure in water and the orientation of the dipole in the strong field of the ion. The extent and total effect of hydration is considered a reflection of the relative sizes of these regions.

Samoilov⁶ stresses that the assumption of definite stoichiometry is only a crude approximation, and supports a model of

continually exchanging water molecules. Energy calculations are based on the action of the ions on the translational motion of the nearest water molecules.

III. Proposed Methods of Measuring Hydration Numbers

Various methods are based on transport phenomena:

A. The difference in the amounts of water transported by the anions and cations can be calculated from a modification of the Hittorf method for measuring transport numbers.²

B. Diffusion coefficients of concentrated electrolytic solutions are interpreted in terms of the sum of the hydration numbers of the two ions.²

C. Ionic mobilities are also interpreted in terms of hydration numbers. The advantage of this method is that values are obtained for individual ions.¹

Numerous methods use thermodynamic calculations to estimate the effect of hydration on equilibrium properties:

D. The solubility decrease of a non-electrolyte (salting-out effect) caused by the addition of an electrolyte reflects the amount of free water which is "tied up" by the added ions.⁷

E. Deviations of the solutions from Raoult's law and the Debye-Huckel theory are used to calculate hydration numbers.² However, this method attributes all deviation to hydration, whereas other inestimable factors undoubtedly also contribute.

F. The rapid rise of the acidity function of strong acids with increasing concentration is attributed to hydration of the proton beyond H_3O^+ .⁸

G. Entropies of dissolved salts are obtained rather easily from experimental data, and are used to determine the hydration trends for families of ions.⁴

Two direct approaches should be mentioned:⁷

H. The effect of the addition of electrolyte on the total volume of solution is used as a measure of hydration.

I. The assumption that the water molecules immediately surrounding the ions are at maximum density serves as a basis in using compressibility data for estimating hydration numbers.

Isotope exchange,⁷ Raman spectra,⁹ nuclear magnetic resonance,¹⁰ x-ray spectra,^{11,12} ultra violet spectra,¹³ surface properties,¹⁴ and rate measurements¹⁵ are also used to give information on the hydration of ions.

IV. Conclusion

The term "ionic hydration number" implies a simple stoichiometric interaction, an idea which is valid for only a few ions. As a result, the energy of hydration is a much more meaningful quantity than is the hydration number. At present several physical pictures of the interaction can be used to explain the effects of hydration.

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1.	Introduction	1
2.	1. The history of the book	2
3.	2. The history of the book	3
4.	3. The history of the book	4
5.	4. The history of the book	5
6.	5. The history of the book	6
7.	6. The history of the book	7
8.	7. The history of the book	8
9.	8. The history of the book	9
10.	9. The history of the book	10
11.	10. The history of the book	11
12.	11. The history of the book	12
13.	12. The history of the book	13
14.	13. The history of the book	14
15.	14. The history of the book	15
16.	15. The history of the book	16
17.	16. The history of the book	17
18.	17. The history of the book	18
19.	18. The history of the book	19
20.	19. The history of the book	20
21.	20. The history of the book	21
22.	21. The history of the book	22
23.	22. The history of the book	23
24.	23. The history of the book	24
25.	24. The history of the book	25
26.	25. The history of the book	26
27.	26. The history of the book	27
28.	27. The history of the book	28
29.	28. The history of the book	29
30.	29. The history of the book	30
31.	30. The history of the book	31
32.	31. The history of the book	32
33.	32. The history of the book	33
34.	33. The history of the book	34
35.	34. The history of the book	35
36.	35. The history of the book	36
37.	36. The history of the book	37
38.	37. The history of the book	38
39.	38. The history of the book	39
40.	39. The history of the book	40
41.	40. The history of the book	41
42.	41. The history of the book	42
43.	42. The history of the book	43
44.	43. The history of the book	44
45.	44. The history of the book	45
46.	45. The history of the book	46
47.	46. The history of the book	47
48.	47. The history of the book	48
49.	48. The history of the book	49
50.	49. The history of the book	50
51.	50. The history of the book	51
52.	51. The history of the book	52
53.	52. The history of the book	53
54.	53. The history of the book	54
55.	54. The history of the book	55
56.	55. The history of the book	56
57.	56. The history of the book	57
58.	57. The history of the book	58
59.	58. The history of the book	59
60.	59. The history of the book	60
61.	60. The history of the book	61
62.	61. The history of the book	62
63.	62. The history of the book	63
64.	63. The history of the book	64
65.	64. The history of the book	65
66.	65. The history of the book	66
67.	66. The history of the book	67
68.	67. The history of the book	68
69.	68. The history of the book	69
70.	69. The history of the book	70
71.	70. The history of the book	71
72.	71. The history of the book	72
73.	72. The history of the book	73
74.	73. The history of the book	74
75.	74. The history of the book	75
76.	75. The history of the book	76
77.	76. The history of the book	77
78.	77. The history of the book	78
79.	78. The history of the book	79
80.	79. The history of the book	80
81.	80. The history of the book	81
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83.	82. The history of the book	83
84.	83. The history of the book	84
85.	84. The history of the book	85
86.	85. The history of the book	86
87.	86. The history of the book	87
88.	87. The history of the book	88
89.	88. The history of the book	89
90.	89. The history of the book	90
91.	90. The history of the book	91
92.	91. The history of the book	92
93.	92. The history of the book	93
94.	93. The history of the book	94
95.	94. The history of the book	95
96.	95. The history of the book	96
97.	96. The history of the book	97
98.	97. The history of the book	98
99.	98. The history of the book	99
100.	99. The history of the book	100

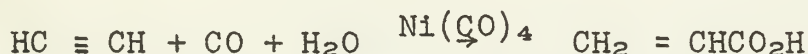
Catalysis of Organic Reactions by Metal Carbonyls

John G. Verkade

December 9, 1958

The metal carbonyls of the first transition series are the most important and interesting members of this group of compounds from the point of view of both applications in organic chemistry and the existence of complexes containing metal, carbon monoxide and organic groups in the same molecule.

The reaction between metal carbonyls and acetylene was discovered by Reppe (1) in 1939. Catalytic quantities of nickel carbonyl were used to effect the synthesis of acrylic acid and its derivatives from acetylene, carbon monoxide and water. Amines and alcohols can also be used instead of water as active

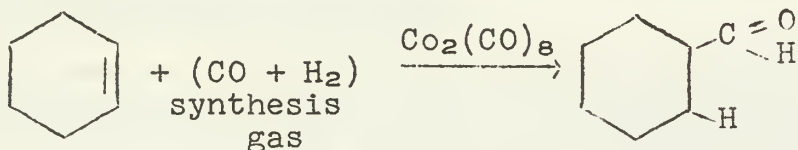


hydrogen compounds to produce the amides and esters, respectively.

In the discussion of the mechanisms of two of the type reactions listed below, special attention will be devoted to the nature of the complexes, which presumably form as intermediates.

Type Reactions Catalyzed by Metal Carbonyls

1. Hydroformylation (1) ("oxo" reaction). A hydrogen and a formyl group are added across a double bond in the presence of cobalt octacarbonyl.



2. Hydrohydroxymethylation (2). In this reaction a hydrogen and a hydroxymethyl group are added across a double bond. This reaction is believed to occur in two steps: (a) a hydroformylation and (b) a reduction of the aldehyde group to an alcohol. The mechanism of this reaction differs in several ways from the hydroformylation reaction (a) in that Fe(CO)_5 is used in place of $\text{Co}_2(\text{CO})_8$ as the catalyst, (b) the reaction is carried out in aqueous base rather than in organic solvents and (c) water instead of hydrogen gas serves as the source of H atoms.

3. Hydrocarboxylation (1). This reaction is carried out using Ni(CO)_4 as shown in the Reppe reaction (vide supra).

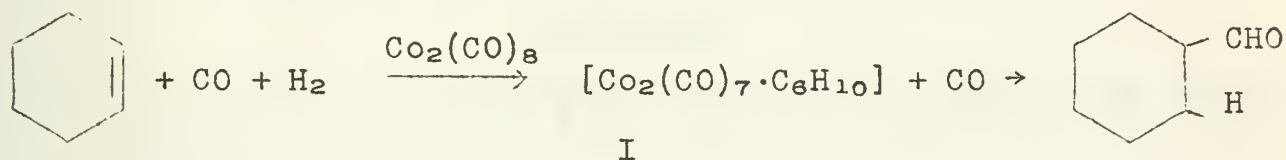
4. Hydroesterification (3). This reaction is also carried out under Reppe reaction conditions except that $\text{Co}_2(\text{CO})_8$ and alcohol are used instead of Ni(CO)_4 and water.

5. Hydrocyanation (4). Hydrogen cyanide is added across a double bond in the presence of $\text{Co}_2(\text{CO})_8$. Little is known of the intermediate products.

The Hydroformylation Reaction

1. Mechanism and Intermediates in Olefin Reactions.

On the basis of the difference in rates of reaction with varying carbon monoxide and hydrogen pressures, it was postulated (5,6,7) that the first step in the reaction entails formation of the complex (I) between the catalyst and the olefin. On the basis of the kinetics, Wender (1) postulated that I reacts



with H_2 to form a second complex II (i.e., $\text{H}_2[\text{Co}_2(\text{CO})_7 \cdot \text{C}_6\text{H}_{10}]$). Some possible structures of I and II will be discussed in the light of experimental evidence (8,9). It is found that $\text{HCo}(\text{CO})_4$ plays an important role in these mechanisms (9,10,11). Support for the existence of II arises from olefin isomerization experiments (1).

2. Mechanisms and Intermediates in Acetylene Reactions.

Tirpak et al (12) followed the reaction kinetics of hexyne-1 and hexyne-2 with $\text{Co}_2(\text{CO})_8$ by measuring the rate of CO evolution. Their interpretation of the mechanism is based on the possible existence of a stable and an unstable form of $\text{Co}_2(\text{CO})_8$ in equilibrium. Possible structures are discussed for the postulated intermediates in the simplest mechanisms fitting all the experimental data.

The Hydrohydroxymethylation Reaction

The importance of the $[\text{H}_2\text{Fe}_2(\text{CO})_8]^+$ ion and the $\text{H}_4\text{Fe}_2(\text{CO})_8$ molecule is emphasized in their roles as isomerization and reduction catalysts. The fact that the hypothetical intermediates in this reaction are isoelectronic with those in the hydroformylation reaction lends support to the similarities in the reaction mechanisms and products.

Recent Work on Organo-Metal Carbonyl Complexes

That the postulation of structures for intermediates in these reactions is dangerous and misleading is clearly demonstrated by the X-ray determination of the structure of $[\text{H}_2\text{Fe}_2(\text{CO})_8 \cdot \text{CH}_3\text{C}\equiv\text{CCH}_3]$ (13). The structure is quite different from any of the proposals made heretofore (14,15,16).

Jonassen (17) has found that a complex between $\text{HCo}(\text{CO})_4$ and butadiene forms which is diamagnetic, has no acidic hydrogen and is monomeric. A possible structure is not given although an X-ray investigation is now in progress.

Sternberg (18) has postulated a structure for the complex formed between $\text{Fe}(\text{CO})_5$ and $\text{CH}_3\text{C}\equiv\text{CCH}_3$. The suggested structure contains a quinone. If correct, this would be a molecule in which the carbon skeleton is formed during the reaction. Duroquinone is

Conclusion

The use of structures of intermediates postulated on the basis of evidence excluding X-ray determination must be limited to understanding the course of the reaction only. It will be recognized that the actual structure may be very different from that postulated. It must also be realized that the interpretation of the mechanisms of these reactions may undergo radical alterations as further structure determinations of such intermediates are carried out.

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Mitsuru Kubota

December 16, 1958

I. Introduction

Infrared spectroscopy has been firmly established as a method for the elucidation of molecular structure chiefly by the empirical correlation of absorption bands to certain atomic groupings and more recently by the study of absolute intensities of these bands. Since the infrared spectrum reflects vibrational energy transitions within the molecule (intramolecular) as well as between molecules (intermolecular), it is not at all surprising that spectral variations occur upon changing the state of a sample. In the transition from gas to liquid to solid, variations in spectra such as differences in relative intensities and positions of bands, splitting of broad bands into several sharp components and apparently new bands appearing in one state, absent in the others, are often detected.^{1,2}

II. Experimental methods

The primary difficulty in obtaining solid spectra is due to the loss of incident radiation by reflection and scattering. Quantitative studies often encounter difficulties in controlling sample thickness, and in evaluating particle size and particle size distribution.¹ Among the more common methods which are employed are the following:

A. Mulling techniques. The solid sample is ground in an agate mortar, and is mixed with high boiling petroleum (Nujol). The mull obtained is then placed between salt plates. Adequate coverage of the spectrum is attained by the use of other mulling materials such as fluorinated hydrocarbon (fluorolube) or hexachlorobutadiene.¹

B. Alkali metal halide disks. A small quantity of sample is ground and mixed with 150 to 200 times its weight of finely powdered KBr or other alkali metal halide. The mixture is placed in a special die, evacuated and pressed for several minutes to yield a clear pellet.⁴⁻⁶

C. Single crystals. The spectrum of a crystal can be taken directly, or if necessary it can be cleaved prior to analysis.⁷ Small crystals can also be studied by mounting them at the focus of a reflecting microscope.⁸

D. Solid films. The spectrum of a solid can be obtained by pouring its melt on a supporting plate upon which it solidifies. More often a solid film is obtained by subliming or crystallizing the solid upon a cold plate.⁹ Better resolution is often obtained by "tempering" the solid film.¹⁰ In the matrix isolation method the gaseous sample and suitable inert matrix is sprayed on a cold surface.

II. Some characteristics of infrared spectra of solids

Except in instances where hydrogen bonding is involved, the spectra of solids obtained with low resolving instruments show only

The purpose of this course is to provide a thorough understanding of the principles of physics. The course is designed for students who have completed the equivalent of high school physics and who are interested in pursuing a career in science or engineering. The course will cover the following topics: mechanics, electricity and magnetism, optics, and modern physics. The course is divided into two semesters. The first semester covers mechanics and electricity and magnetism. The second semester covers optics and modern physics. The course is taught by Professor [Name], who is a leading expert in the field of physics. The course is highly interactive, with a strong emphasis on problem-solving and laboratory work. Students are encouraged to participate in class discussions and to work on problems in groups. The course is also supported by a variety of resources, including textbooks, lecture notes, and laboratory manuals. The course is highly recommended for students who are interested in physics and who want to gain a deep understanding of the subject.

2. Course Objectives

The course objectives are to provide students with a solid foundation in the principles of physics. The course is designed to help students develop the following skills: understanding of the basic principles of physics, ability to apply these principles to solve problems, and ability to communicate scientific ideas. The course is also designed to help students develop the following attitudes: curiosity, creativity, and a sense of responsibility. The course is highly interactive, with a strong emphasis on problem-solving and laboratory work. Students are encouraged to participate in class discussions and to work on problems in groups. The course is also supported by a variety of resources, including textbooks, lecture notes, and laboratory manuals. The course is highly recommended for students who are interested in physics and who want to gain a deep understanding of the subject.

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minor variations.¹¹ Greater resolution however, shows a wealth of fine components, which are markedly different from those of the liquid or gaseous states. Much current research is focused at the lack of satisfactory explanations for many spectral features of the solid state. Some aspects of solid state spectra which have been fairly well demonstrated are to be discussed.

As a consequence of the close order crystal environment, intermolecular effects are greatly enhanced in the solid state. With polar compounds dipole-dipole interactions often lead to spectral changes. Induced absorptions which do not highly depend on polarity may persist, in which case they are intensified, or may vanish when a liquid is crystallized. Such absorptions have been ascribed to dipole moments induced by intermolecular forces in clusters of interacting molecules.^{12,13}

Splitting of bands throughout the crystal spectrum result from combination bands between internal modes and lattice torsions. This effect, also known as librational interaction, can account for most of the complex fine structure of an absorption band.^{14,15} First order theory and methods for formulating selection rules in terms of crystal symmetries have been developed and well demonstrated.^{16,17} Recent low temperature studies highly support this theory of librational interaction.^{6,18}

Alterations in crystal lattice, such as changing from one polymorphic form to another, which lead to changes in the immediate environment of vibrating groups, often cause spectral changes. Rotational isomers which exist in the liquid and gaseous states are often eliminated in the solid state.^{1,11}

Orientation effects become more pronounced in the solid state due to the increased orderly arrangement of molecules. If the molecules are lined up in a manner such that the electric vector associated with some localized group vibration lies along the axis of a partially polarized beam of radiation, the expected absorption band can be weak or even absent.¹

The Christiansen filter effect (anomalous reflection and transmission) often occurs in molecular and ionic crystals. Peaks associated with this effect are much closer together for molecular crystals, since they are produced by a single frequency instead of a wide band of lattice frequencies.¹⁹

IV. Some applications.

A. Chemisorbed molecules. Infrared investigations of molecules chemisorbed on solids give information on the structures of intermediates involved in heterogeneous catalysis. Radiation losses by scattering and absorption are minimized by dispersing the small metal particles in supporting silica or alumina, or by using evaporated metal films. Carbon monoxide adsorbed on platinum films exhibits a band at 2050 cm^{-1} similar to that in nickel carbonyl, thereby suggesting a "linear type" Pt-C-O bond. Carbon monoxide adsorbed on silica supported palladium shows peaks at 1820 and 1925 cm^{-1} , similar to peaks in $\text{Fe}_2(\text{CO})_9$. This suggests "bridge type" linkages.²⁰ Eischens concludes that such infrared studies provide a precise means of distinguishing

between chemisorption and physical adsorption.²¹

B. Matrix Isolation. Leisurely spectral study of extremely unstable species, even free radicals, can be accomplished by this method.²² That mechanisms of reactions can often be elucidated, is shown vividly in a study of the photolysis of nitromethane and subsequent detection of nitroxyl.²³ Spectral studies of hydrogen bonding effects have been illuminated by the matrix isolation method as a consequence of reduced band widths which aid in the detection of overlapping and accidentally degenerate bands.²⁴

C. Structural studies with polarized radiation. Quantitative treatment of results of polarized infrared studies can often complement structural information obtained by x-ray diffraction. Using this method, along with isotopic substitutions, L.H. Jones has worked out complete fundamental assignments for solid complex cyanides, such as $\text{KAu}(\text{CN})_2$, $\text{KAg}(\text{CN})_2$ and $\text{K}_3\text{Cu}(\text{CN})_4$. Calculations of stretching force constants indicate that the metal is bonded to the carbon rather than the nitrogen atom.²⁵

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ELECTRON TRANSFER AND HETEROGENEOUS CATALYSIS

C. H. Travaglini

January 13, 1959

I. Introduction

The theoretical approach to surface catalysis was first considered in a series of chemical papers in the early 1930's by Langmuir, who suggested that adsorption occurred by chemical forces. Solid state theories can be used as a first approximation to correlate catalytic activity with solid state behavior, if the differences of bulk solid and surface are considered. The nature of the adsorbed film on metals, the reaction path and activated complexes involved will be examined, and related oxide studies considered.

II. The Solid and the Activated Complex

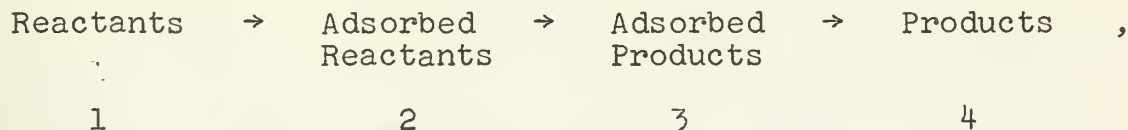
Catalytic influence may be divided into two factors, geometric and electronic. (1) The geometric factor involves fitting the substrate (adsorbate) to either one atom (single-point adsorption) or several points simultaneously (Multiplet Theory) of the catalyst surface. (2,3) The two factors cannot strictly be separated, since the bond length between the two surface atoms is characteristic of the bond concerned, but attention here will focus on the electronic factor.

The two main theories of metals help correlate the electronic factor with catalytic activity, which, in a metal, depends on the electronic work function, electron density gradient, and the electron density at the Fermi surface. (4,5) The energy band theory of Bloch and Brillouin visualizes the valence electrons of metals moving freely through a lattice of positive cores, providing a periodic potential field, arising at the surface. The energy of the electron remains quantized, but overlapping energy levels form allowed energy bands, separated by gaps of non-allowed energy, limited by the energy of the Fermi surface (highest filled electron level at 0°K.) (6) Electron conductivity occurs if a band (Brillouin zone) is partly full, as only an electron in a singly occupied level can migrate in an external field. If the band is full or the energy gap between zones is too great, semiconductors or insulators result. In the transition metals, the nd and (n+1)s levels broaden and overlap, leaving unfilled holes in the d-band of approximately .6/g-at.

The Pauling resonating-valence-bond theory describes a metal in terms of hybrid electron-pair bonds, resembling ordinary covalent bonds. (7,8) Metallic properties are based on possession of all or some atoms in a given metal of a free orbital which allows uninhibited or unsynchronized resonance, as in $\text{Li-Li} \rightarrow \text{Li}^{\oplus}\text{Li}^{\ominus}$. Some d-orbitals in the transition metals remain unhybridized, as atomic orbitals, which can be used in chemisorption. Here again ferromagnetic saturation moments reveal .6 unpaired d electrons per gram-atom.

The energy of bond formation may be calculated using Lennard-Jones potential energy curves. (9, 10) For a maximum free energy change, the substrate particles must be in a geometric site with minimum activation energy necessary for adsorption, and with the binding electrons in suitable electronic orbitals, as in the crystal-lite planes of least packing density, 111 or 110. (11) The rates of

heterogeneous chemisorption reactions, controlled by the formation of a bound complex, are examined using the Polanyi profile method:



assuming 2→3 as the rate determining step. Examination of these curves reveals factors for decreasing the energy of activation and hence increasing rate.

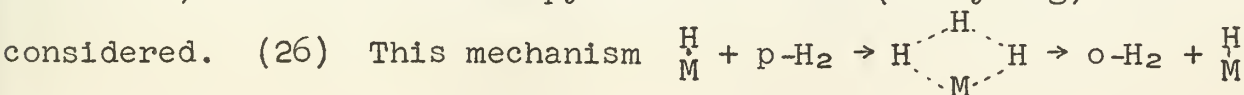
III. Chemisorption and Chemical Reactions on Metals and Oxides

Early experimental work by Schwab on formic acid decomposition on alloy catalysts indicated a link between the energy of activation and the energy necessary to remove an electron from the substrate to the Fermi level of the metal. (12) By adding mult-valent metals to monovalent ones, thereby increasing the energy of the Fermi surface, the activation energy for decomposition increases as expected. (4) Hydrogenation catalyzed on transition metals revealed this same dependence on atomic d- orbitals. Eley and Couper found in their investigation of the para-H conversion on Pd-Au alloys that the empty d-orbitals could come to the catalyst surface, accept electrons, and form low energy complexes. (13) Oxide semiconductors of the n-type favor H₂, CO and substances which donate electrons, while p-types favor electron-acceptor substrates, such as N₂O. (14) In general, electron excess lattices favor dehydrogenation, but electron defect lattices favor dehydration. (10)

Chemisorption involves metal half-bonds, similar to those in electron-deficient compounds, so that depending on the crystal lattice and plane exposed, single or multiple bonds (M-H, M=O, M≡N) may form. (19) Trapnell found that all sp and dsp-bonding metals adsorb O₂ except gold, and only dsp metals adsorb N₂, H₂, CO, C₂H₄ and C₂H₂. (8) The heat of chemisorption as calculated by Eley decreases as the fraction of surface covered increases. (6, 15) The field emission microscopy studies of Gomer reveal a primary mobile film and a secondary stationary film of adsorbate, with different energies of activation. (16)

Suhrmann's examination of electronic work functions as a measurement of electronic interaction on a metal surface shows that O₂, N₂, N₂O and CO require surfaces with low work functions (easily release electrons), but H₂ adsorption favors a high work function. (21) Even saturated hydrocarbons adsorb at low temperatures on metals by electron release as shown by the decrease in work function.

For the elucidation of mechanisms for catalytic reactions on metals, the energy of activation and frequency factor (E, A of Arrhenius) or heat and entropy of activation (of Eyring) must be



for the para-H conversion on W and Pd-Au is consistent with the ΔE^\ddagger involved. (13, 17, 18) Abruptly at .6 atomic percent of Au in Pd, the ΔE^\ddagger increased, perhaps indicating a change to the Bonhoeffer-Farkas mechanism, $2M-H \rightarrow M-H + o-H_2$, simultaneously with the filling of the d- orbitals. (20) Dowden and Reynolds support the relationship of activity with the number of d-holes with their dehydrogenation work on binary solid solutions of Group VIII and Ib elements. (4) The efficacy of styrene dehydrogenation on a Ni-Cu alloy series decreases as the number of d-holes approaches zero, as the Cu concentration increases. Further correlation comes with Trapnell's results indicating the transition metals W, Ta, Mo, Ti, Zr and Fe as more active for chemisorption. (22)

Adsorption on oxide surfaces involves electron transfer between the adsorbate and defects near the surface. Water often helps promote reactions, especially on insulators, such as Al_2O_3 . Propylene isomerization reaches a maximum at 85% SiO_2 with Al_2O_3 , the point of maximum acidity (greatest H-ion activity). (23) Heating in hydrogen or adding Ga_2O_3 increases ZnO activity, possibly by formation of surface anionic defects, such as OH^- . Oxygen lattice exchange studies on Cu and Zn oxides by Winter show a lack of equilibration and oxide formation, suggesting that reaction occurred on interstitial metal atoms, which then may have diffused into the catalyst interior rendering the dissociation irreversible. (24) The oxidation of SO_2 by metal ions also depends on the ability of the cation to transfer electrons, possibly via a radical-ion mechanism. (25)

IV. Conclusion

For the type and intensity of electron interactions between metal surfaces and adsorbed molecules, the factors which must be considered are the magnitude of the work function, the electron affinity of the species to be adsorbed, the asymmetry of the electronic configuration, the presence of unpaired and π -electrons, and the effects due to steric hindrance. (21) Changes in the activation energy for adsorption depend on the electron concentration, or on the degree of completion of the Brillouin zone, indicating that the main process in heterogeneous catalysis is the formation of adsorbed layers by electron sharing.

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THERMAL DECOMPOSITION OF THE NITROGEN OXIDES

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February 10, 1959

I. Introduction

The thermal decomposition of the nitrogen oxides is of great interest for several reasons. The primary reason may be summed up in the following quotation (1): "Although examples are fewer, the oxides of nitrogen with oxygen atoms, molecules, and ozone illustrate almost as many principles of reaction kinetics as do all gas-phase organic reactions. These reactions form a family of their own with many elementary reactions appearing in more than one system."

Another extremely important reason is the fact that the phenomenon of nitrogen fixation has not been completely explained. Work on the kinetics of the thermal decomposition of the nitrogen oxides, coupled with photochemical studies, promises to give an insight into this problem.

II. Bond "Energies"

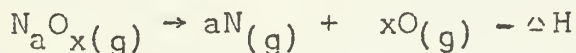
In any kinetics study a knowledge of the bond energies of the reactants and products is helpful. Bond energies for some of the nitrogen oxides are listed in Table I.

Table I

Bond Energies

Compound	<u>B(N-O) kcal/mole</u>	<u>B(N-ON) kcal/mole</u>	<u>B(N-N) kcal/mole</u>
NO	123		
NO ₂	98		
N ₂ O ₄	99		13.8
NO ₃	82		
N ₂ O ₅	90	21.6	

They are defined as follows:

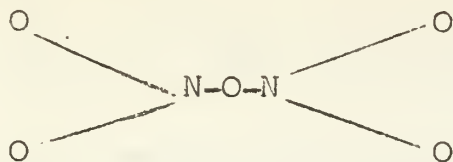


$$B(N-O)_{N_a O_x} = \frac{\Delta H}{x} \quad a = 1$$

with appropriate modifications for $a \neq 1$.

Using these bond energies, one can predict qualitatively the path of reaction when two or more alternative paths are given.

The decomposition of N_2O_5 into NO_2 and NO_3 gives an example of the use of bond energies. If we assume that the structure of N_2O_5 can be written as



we can picture the decomposition as the breaking of the N-O-N bond in an appropriately excited state. The activation energy involved in this reaction should be roughly equivalent to the energy involved in the breaking of the bond. Such is, indeed, the case (2).

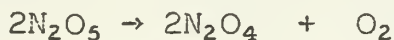
In other cases postulated mechanisms may be ruled out if the energy of activation is known and one can assume some reasonable value for the energy of the bond to be broken. If these two are widely different, the proposed mechanism can usually be discarded.

III. General Experimental Methods

A few of the many experimental techniques which have been used in this field are discussed below with particular reference to the methods for determining concentrations.

A. Direct Pressure Measurements.

The classical study of the decomposition of nitrogen pentoxide is that of Daniels and Johnston and of Daniels and other co-workers(3). This reaction obeys the stoichiometry



The important feature of the apparatus employed in this study was the device used to measure the pressure within the reaction vessel. A platinized glass diaphragm separated the reaction vessel from an outer space, the pressure in which could be measured by a mercury manometer, and could be adjusted to a predetermined pressure at will. When the pressure in the reaction vessel was equal to, or greater than that outside, the diaphragm made electrical contact with a platinized glass knob. The pressure on the outside of the diaphragm was increased, and the time for the inside pressure to reach the new value and cause a deflection of a galvanometer was noted with a stopwatch. This procedure was followed until no further change was noted. The dissociation of N_2O_4 somewhat complicates the pressure readings, but it can be taken into account.

B. Spectroscopic Methods:

1. Kaufman and co-workers have used the following technique in the decomposition of nitric oxide (4). In runs where the % decomposition was greater than 30%, excess oxygen was added to convert all of the remaining NO to an equilibrium mixture of nO_2 - N_2O_4 . When the % decomposition was small, excess NO was added to convert all the oxygen formed in the decomposition to an equilibrium mixture of NO_2 , N_2O_4 and N_2O_3 . The samples containing

excess oxygen were analyzed at 3000 and 3200 Å since the absorption coefficient of N_2O_4 is "roughly" twice that of NO_2 and no account need be taken of the $NO_2-N_2O_4$ equilibrium. Samples containing excess NO were analyzed at 3450, 3500, 3550, and 3600 Å so that the variable N_2O_3 could be taken into account.

2. Hisatsune, Crawford, and Ogg have followed the $NO-N_2O_5$ reaction using a fast-scanning spectrometer (5). This instrument can be used if the reaction has a half-time of about one second when two neighboring bands of different molecular species are being used or if the half-time is as low as 0.1 second when only one band is being utilized. In the $NO-N_2O_5$ reaction, the N_2O_5 absorption at 1750 cm^{-1} and the NO_2 absorption at 1616 cm^{-1} were used.

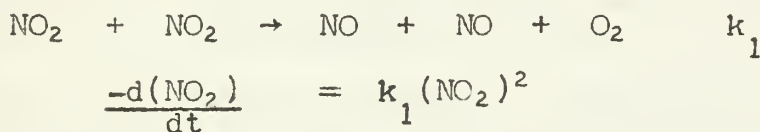
C. Shock Tube Method

The shock tube pyrolysis of N_2O_5 has been reported by Schott and Davidson (2). In this technique a shock wave is produced in N_2O_5 by argon and the NO_2 and NO_3 produced are measured spectrophotometrically. The time required for the dissociation of N_2O_5 is of the order of 5 μ sec at 600° K. The subsequent decomposition of NO_3 , which is slow compared with the dissociation, can also be followed.

IV. Examples:

A. Thermal Decomposition of NO_2 :

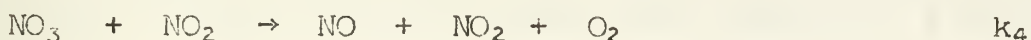
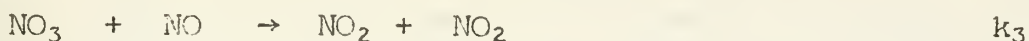
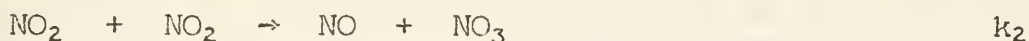
The thermal decomposition of NO_2 was first investigated by Bodenstein in 1922 (6). He found that the reaction followed second order kinetics and could be written as:



Measurements in 1956 by Rosser and Wise (7) using a spectrophotometric method of analysis and concentrations in the range 10^{-7} mole/cc. (~ 6 mm Hg) confirmed the earlier work and gave the following expression for k_1 :

$$k_1 = 10^{12.6} \exp(-26,900/RT) \text{ cc mole}^{-1} \text{ sec}^{-1}$$

However, Ashmore and Levitt, working at lower pressures (~ 3.3 mm Hg) near 400°C, have found anomalously high initial rates for the decomposition (8). The slope of a plot of $1/(NO_2)$ vs. time falls steadily and then remains constant for a considerable time. The same result was obtained when higher initial pressures were used, but the limiting slope was attained more rapidly. This non-linearity was completely suppressed by the addition of an equal pressure of NO ; but N_2 up to 0.5 atmosphere had no effect. Ashmore and Levitt proposed the following mechanism:



All of these steps except (2) have been invoked in a discussion of the kinetics of the N_2O_5 decomposition or reactions of the pentoxide. Assuming the steady state treatment for NO_3 , the following is obtained:

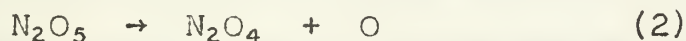
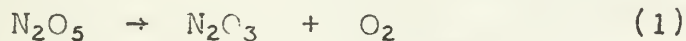
$$\frac{d}{dt} \frac{1}{(\text{NO}_2)} = \frac{-1}{(\text{NO}_2)^2} \frac{d(\text{NO}_2)}{dt} = (k_1 + k_2) \frac{-k_2 k_3 (\text{NO})}{k_3 (\text{NO}) + k_4 (\text{NO}_2)} \quad (5)$$

Using this rate law it is seen that early in the reaction when (NO) is small, plots of $1/(\text{NO}_2)$ vs. time will have slope $(k_1 + k_2)$; and that later, if $k_3 \gg k_4$ and $k_1 \gg k_2$, $k_3(\text{NO})$ rapidly becomes much greater than $k_4(\text{NO}_2)$ and the slope becomes k_1 , which can be identified with the normal value for the rate constant of the decomposition. The effect of added NO is to make $k_3(\text{NO}) \gg k_4(\text{NO}_2)$ from the beginning. The mechanism is also consistent with the observation that the addition of N_2 has no effect on the initial rate.

3. Thermal Decomposition of N_2O_5 (9).

The study of the decomposition of nitrogen pentoxide has played an important role in the development of gas kinetics. First investigated by Daniels and Johnston(3), this decomposition was, until 1925, the only accepted example of a first-order gas reaction. The reaction was subsequently studied over a wide variety of temperatures and pressure by other workers using many different techniques. These investigations were in substantial agreement with Daniels and Johnston's results.

If the reaction is unimolecular, the immediate products of the decomposition must react further since the stoichiometry refers to two molecules of NO_2 per molecule of N_2O_5 . Several possibilities exist for the initial decomposition:

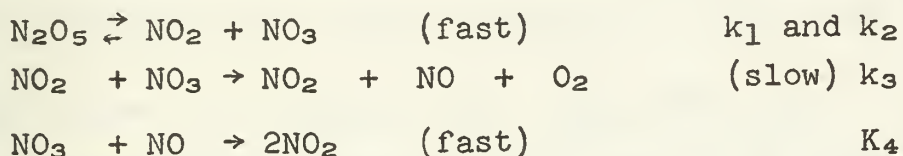


The first can be ruled out because it involves a change in the electron multiplicity in the initial step and thus is presumably very slow. The second has a ΔH which is endothermic by 11 kcal. E_a , however, is only 24.6 kcal, and the ΔH for the rate-determining step cannot exceed this. Reaction 3 has a ΔH of 24.3 kcal. in good agreement with the experimental value and was thus accepted as the initial step for quite some time.

The low pressure investigation of this decomposition showed that it remained first order down to 0.05 mm. At lower pressures

the apparent order with respect to N_2O_5 increased to a value of 1.8 at 10^{-3} mm (10). This change in order is in accord with the Lindemann theory, except that it takes place at much too low a pressure. Using even the most favorable assumptions as to the molecular diameter and the number of degrees of freedom contributing to the vibration of the molecule, calculations showed that the rate constant should have been appreciably changed at a pressure of 0.1 mm.

In 1947, Ogg showed that the experimental data could be explained by the following mechanism (11):



Using the steady state assumption for (NO_3) the rate of decomposition of the pentoxide is

$$\frac{-d(N_2O_5)}{dt} = \frac{2k_1k_3(N_2O_5)}{k_2 + 2k_3} = \frac{2K_1K_3(N_2O_5)}{k_2}$$

This reaction is not unimolecular at all on this basis but involves a prior equilibrium presumably with a third body followed by a bimolecular rate-determining step.

This mechanism predicts the falling-off of the rate constant at low pressure since the unimolecular dissociation of N_2O_5 into NO_2 and NO_3 is governed by activation through collision, and at very low pressures the rate will become equal to the rate of activation by collision.

Presumed proof of this mechanism has been offered by several investigators. Ogg has substantiated it by investigating the exchange between $N_2^{15}O_5$ and NO_2 . The rate constant for this reaction should be k_1 and should fall off as the total pressure is decreased. This was observed experimentally (12). The reaction of NO with N_2O_5 should offer an alternative approach to determining k_1 since the mechanism for this reaction contains k_1 as the slowest step. Mills and Johnston (13), Hisatsune, Crawford and Ogg (5), and Jach (14) have separately confirmed this...

Further support for the Ogg mechanism comes from the spectroscopic identification of NO_3 in the pentoxide-catalyzed decomposition of ozone (15), and by the fact that the NO_3 intermediate can explain quantitatively the oxidation of NO by O_3 , the reaction of N_2O_5 with NO and the decomposition of ozone catalyzed by N_2O_5 (16). In addition, the shock tube experiments of Schott and Davidson have given direct measurement of the equilibrium between N_2O_5 , NO_2 , and NO_3 and have explained the subsequent decomposition of NO_3 (2).

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February 24, 1959

I. Introduction

The electron-pair bond is used as the basic model to explain the chemical combination of atoms into molecules. There are numerous compounds, however, in which the number of bonds required to connect all the atoms is greater than the number of valence electron-pairs available from the participating atoms. Many simple compounds of this type can be explained in terms of a "three-center bond" in which one electron pair binds three atoms together instead of two. In more complex compounds of this type, the three-center bond is generalized into molecular bonds through the method of molecular orbitals. This theory gives a satisfactory, qualitative picture for the existence and stability of these compounds.

II. The Three-center Bond

Consider two atoms ($_1$ and $_2$) of the same element and an atom ($_3$) of the same or a different element being positioned relatively near each other so that they must be considered to be bonded together. If there are just two valence electrons (assuming also that no atom has unshared pairs to donate) among the three atoms, the conditions for the formation of the three-center bond would be met. This bonding is best described by the linear combination of atomic orbitals (the L.C.A.O. method). (1)

The energy levels obtained from the linear combination of two suitable atomic orbitals into new orbitals is given by:

$$E_{\pm} = E_0 + \frac{H_{12} + ES_{12}}{1 + S_{12}}, \text{ where } E_0 \text{ is the}$$

original energy of the two separate atoms which must be similar, H_{12} is the "resonance integral", which is a measure of the interaction between the two orbitals 1 and 2, S_{12} is the "overlap integral" of the two orbitals; since H_{12} possesses a negative value, the lowest energy of the system is given by E_{+} which would be the bonding orbital.

In the treatment of three orbitals (2,3), it is first assumed that S_{12} is a constant and that $H_{12}=H_{23}=H$ and that $H_{13}=G$. By the variational method of calculation, the energy of this system can be given by:

$$E_{+} = H_0 + G/2 + [(G/2)^2 + 2H^2]^{1/2}$$

$$E_0 = H_0 - G$$

$$E_{-} = H_0 + G/2 - [(G/2)^2 + 2H^2]^{1/2}$$

By comparing the relative values of E_{+} , E_0 , and E_{-} at $H/G = 0$, $G/H = 0$, and $G/H = 1$, we arrive at one bonding level (E_{+}) and two antibonding levels. There are only two electrons, however, so the

bonding level (E_+) is exactly filled, and thus one electron-pair binds all three atoms. At $G/H = 0$, it is called an "open three-center bond" and at $G/H = 1$, it is called a "central three-center bond".

The orbitals combined by this method must be of the same relative energy, of the same symmetry along the bond axis or plane, and orthogonal. Consider diborane with boron atoms B_1 , B_2 and bridge hydrogens H^1 and $H^{1'}$. The four orbitals obtained by combining the atomic orbitals (4) are:

$$\psi_1 = (\sigma_1 + \sigma_2 + s^1 + s^{1'})/2$$

$$\psi_2 = (p_1 + p_2 + s^1 - s^{1'})/2$$

$$\psi_3 = (\sigma_1 + \sigma_2 - s^1 - s^{1'})/2$$

$$\psi_4 = (p_1 + p_2 - s^1 + s^{1'})/2$$

where σ is the 2S orbital of boron, s is the 1S orbital of the hydrogens, and p is a suitable 2P orbital of boron perpendicular to the boron-boron bond axis. ψ_1 and ψ_2 are bonding orbitals; the latter two are antibonding. It is now possible to take linear combinations of these orbitals. The two bonding orbitals are given by:

$$X_1 = (\psi_1 + \psi_2) / \sqrt{2}$$

$$X_2 = (\psi_1 - \psi_2) / \sqrt{2}$$

By algebraic substitution and rearrangement, it can be seen that X_1 and X_2 are composed of $(\sigma_1 + p_1) / \sqrt{2}$, $(\sigma_2 + p_2) / \sqrt{2}$, and the S orbitals of the hydrogens. These terms would also result if the boron orbitals are considered to be SP hybrids. Thus the linear combination of pure S or P or even SP hybrids leads to stable electronic configurations for diborane. This approach can be extended to the higher boron hydrides and the other electron deficient compounds.

III. Metal Alkyls (5)

It has been found that metal alkyls such as $Al(Me)_3$, $Al(Et)_3$, $Be(Me)_2$, and $Ga(Et)_3$ exist as dimers. (6)

Compounds such as (Me_4Pt) , (Me_3ClPt) , and (Me_3In) are tetrameric in the solid state (7,8). Since there are not enough conventional electron-pairs available in these molecules to form such polymers, bonding must be explained by the three-center bond (9,10). It is postulated that when an atom with an unoccupied bonding orbital (usually a metal) is combined with atoms or groups that do not have any unshared pairs (e.g. hydrogen or methyl groups) the atoms will group themselves so that all orbitals are at least partially occupied (11). By forming molecular orbitals from available atomic orbitals, all bonding orbitals can be completely filled. The acute metal-carbon-metal angle measured is thought to be necessary for effective overlap of the metal and carbon SP^3 orbitals.

IV. The boron hydrides

Bonding in the boron hydrides (12,13) is explained (2,3) in terms of open three-center bonds, central three-center bonds, and linear combinations of these to form higher molecular orbitals embracing the framework of boron atoms. They are all fragments of an icosahedron or an octahedron.

All hydrides of boron are members of two homologous series with the formulas B_nH_{n+4} and B_nH_{n+6} . Two new hydrides B_6H_{10} and B_9H_{15} have recently been isolated (14) and their structures determined (15, 16). The structures of the boron hydrides have been investigated mathematically by a topological approach. Predictions have been made concerning the existence of other possible hydrides (17).

V. Other Boron Polyhedra

The atoms in elemental boron are arranged to form an icosahedral structure. There are three crystalline modifications (18) containing 12, 50 and 108 atoms of boron per unit cell which means 1, 4 (plus 2 boron atoms), and 9 icosahedra respectively in the unit cell. The bonding is explained (19) in terms of molecular orbitals consisting of 13 bonding orbitals. The boron atoms donate 24 electrons; so two electrons must come from other icosahedra or boron atoms (20,18). Boron also forms an icosahedral network in boron carbide $B_{12}C_3$ and again must receive two electrons from the carbon chain (19). Boron forms an octahedron in the metal borides MB_6 (21). Here there are seven bonding orbitals and eighteen valence electrons. Six electrons are used in normal single bonds to other octahedra so that two electrons again must come from the metal atom. The boron atoms in B_4Cl_4 , are arranged tetrahedrally with respect to each other; in addition each boron atom is bonded to a chlorine atom (22). A compound with the double molecular weight, B_8Cl_8 , has also been reported and its structure determined (23). It consists of a boron network surrounded by chlorine atoms, but it is not a regular polygon.

VI. Interstitial Phases

R. E. Rundle (24) has considered the bonding in metallic carbides, nitrides, and oxides as "electron-deficient" bonding. The properties and structures of these phases appear to require octahedral bonding for the first row elements, which would mean that there are not enough electrons for all electron pair bonds. The concept of the "half bond" has been advanced by Rundle.

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INDEX

1. General Introduction	1
2. The History of the Subject	2
3. The Scope of the Subject	3
4. The Method of the Subject	4
5. The Results of the Subject	5
6. The Conclusion of the Subject	6
7. The Appendix	7
8. The Bibliography	8
9. The Index	9
10. The Glossary	10
11. The List of Figures	11
12. The List of Tables	12
13. The List of Plates	13
14. The List of Maps	14
15. The List of Photographs	15
16. The List of Drawings	16
17. The List of Diagrams	17
18. The List of Schemes	18
19. The List of Formulas	19
20. The List of Equations	20
21. The List of Theorems	21
22. The List of Lemmas	22
23. The List of Propositions	23
24. The List of Definitions	24
25. The List of Axioms	25
26. The List of Postulates	26
27. The List of Principles	27
28. The List of Laws	28
29. The List of Rules	29
30. The List of Procedures	30
31. The List of Algorithms	31
32. The List of Programs	32
33. The List of Systems	33
34. The List of Models	34
35. The List of Simulations	35
36. The List of Experiments	36
37. The List of Observations	37
38. The List of Measurements	38
39. The List of Calculations	39
40. The List of Computations	40
41. The List of Analyses	41
42. The List of Syntheses	42
43. The List of Designs	43
44. The List of Plans	44
45. The List of Diagrams	45
46. The List of Schemes	46
47. The List of Formulas	47
48. The List of Equations	48
49. The List of Theorems	49
50. The List of Lemmas	50
51. The List of Propositions	51
52. The List of Definitions	52
53. The List of Axioms	53
54. The List of Postulates	54
55. The List of Principles	55
56. The List of Laws	56
57. The List of Rules	57
58. The List of Procedures	58
59. The List of Algorithms	59
60. The List of Programs	60
61. The List of Systems	61
62. The List of Models	62
63. The List of Simulations	63
64. The List of Experiments	64
65. The List of Observations	65
66. The List of Measurements	66
67. The List of Calculations	67
68. The List of Computations	68
69. The List of Analyses	69
70. The List of Syntheses	70
71. The List of Designs	71
72. The List of Plans	72
73. The List of Diagrams	73
74. The List of Schemes	74
75. The List of Formulas	75
76. The List of Equations	76
77. The List of Theorems	77
78. The List of Lemmas	78
79. The List of Propositions	79
80. The List of Definitions	80
81. The List of Axioms	81
82. The List of Postulates	82
83. The List of Principles	83
84. The List of Laws	84
85. The List of Rules	85
86. The List of Procedures	86
87. The List of Algorithms	87
88. The List of Programs	88
89. The List of Systems	89
90. The List of Models	90
91. The List of Simulations	91
92. The List of Experiments	92
93. The List of Observations	93
94. The List of Measurements	94
95. The List of Calculations	95
96. The List of Computations	96
97. The List of Analyses	97
98. The List of Syntheses	98
99. The List of Designs	99
100. The List of Plans	100

James E. Huheey

March 3, 1959

I. CHLORIDES

A. Preparation and Structure

1. Diboron Tetrachloride was first prepared in 1925 by striking an arc between zinc electrodes in the presence of BCl_3 (1). However, because of the low yields and handling difficulties almost 25 years passed before further work appeared. Schlesinger and co-workers prepared B_2Cl_4 by passing boron trichloride vapors at low pressures through an alternating current glow discharge between mercury electrodes(2,3). Holliday and Massey found that yields are improved in the glow discharge method if a direct current is used in place of alternating current(5). A method utilizing microwave excitation has also been developed(4).

From the infra-red and Raman spectra of gaseous and liquid B_2Cl_4 , Wartik and co-workers concluded that the molecule has the symmetry of a non-planar ethylene model(6). Lipscomb and co-workers found by an X-ray diffraction study that the molecule is planar in the solid, with the B-B bond stretched somewhat(7). This difference in structure as determined by these two methods could either reflect an error in the spectroscopic interpretation or the presence of sufficient lattice energy in the solid to twist the non-planar molecule into planarity upon crystallization.

2. Tetraboron tetrachloride is formed in small quantities as a by-product in the preparation of diboron tetrachloride(8). It appears as a yellowish crystalline residue when B_2Cl_4 is volatilized. It decomposes in aqueous basic solution with the liberation of six equivalents of hydrogen per mole. This would indicate six boron to boron bonds and suggests a structure formed of a tetrahedron of boron atoms(8). X-ray studies have shown that this picture is correct and that the chlorine atoms form a tetrahedron around and beyond the tetrahedron comprising the four boron atoms(9).

3. Octaboron octachloride is also obtained as a by-product in the preparation of diboron tetrachloride. The molecule consists of an irregular polyhedron with one boron and one chlorine atom at each corner(10).

B. Reactions of Diboron Tetrachloride

1. Addition Reactions-Diboron tetrachloride forms 1:1 addition compounds with hydrogen sulfide(11) and ethers(3) and 1:2 adducts with ethers(3), thioethers(11), phosphine(11) and tertiary amines(3). The product of the reaction between diboron tetrachloride and trimethyl amine is especially interesting because molecular weight determinations indicate that no structure has as yet been proposed for the addition compound.

2. Replacement Reactions-The chlorine may be replaced easily by various groups through solvolytic processes. The reactions probably proceed via the addition of a base to the Lewis Acid, B_2Cl_4 , followed by loss of chloride ion or hydrogen chloride. Thus

ARTICLE XXXIII

1. The purpose of this article is to provide for the election of a delegate to the American Medical Association from the State of Illinois. The delegate shall be elected by the members of the Illinois Medical Association at its annual meeting. The delegate shall have the right to vote on all matters coming before the association.

2. The delegate shall be elected for a term of one year. He shall be eligible for re-election. The delegate shall be elected by the members of the Illinois Medical Association at its annual meeting. The delegate shall have the right to vote on all matters coming before the association.

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hypoboric acid, $B_2(OH)_4$, or its esters may be produced by reaction of B_2Cl_4 with water or alcohols, respectively(2,3). Likewise, N-substituted amides have been prepared from B_2Cl_4 and secondary amines(3). Reaction with ammonia gives a product of composition $(BNH)_x$, but little is known about its structures(3).

At temperatures below $-78^\circ C.$, hydrogen sulfide forms a normal addition compound with B_2Cl_4 . Above this temperature, further reaction occurs with the formation of BCl_2SH , $B_3S_3Cl_3$, BCl_3 , and other products(11). Trichloroborsulfide is of special interest because of its ring structure(12).

3. Oxidation Reactions-Diboron tetrachloride reacts with chlorine, bromine, and oxygen to give BCl_3 and B_nX_3 (n=oxidation state of X). Mixed halides could not be isolated. No reaction occurs when B_2Cl_4 is treated with iodine, sulfur, or white phosphorus(13). The reaction with cyanogen is complex, yielding a product whose composition corresponds to the empirical formula $B_2Cl_4 \cdot 1.5(CN)$. When heated, BCl_3 is released. Wartik has proposed structural formulas to explain this behavior(14).

II. OTHER HALIDES

Lower iodides have been prepared(15). Treatment of BI_3 with a radio frequency discharge at low pressures yields diboron tetraiodide. The compounds B_xI_y ($x > y$) and $(BI)_n$ have also been reported.

Diboron tetrabromide may be obtained in small amounts, together with a brown-black amorphous powder of variable composition, by glow discharge in a mixture of Ar and BBr_3 (16).

Diboron tetrafluoride has been prepared by treating B_2Cl_4 with antimony trifluoride. It behaves similarly to the chloride, forming etherates and a tetrameric addition compound with trimethylamine(17). Its structure has been shown by an X-ray study to be planar(18).

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1. Introduction	1
2. Theoretical background	2
3. Methodology	3
4. Results	4
5. Discussion	5
6. Conclusion	6
7. References	7
8. Appendix	8
9. Bibliography	9
10. Index	10
11. Glossary	11
12. Acknowledgements	12
13. Declaration of interest	13
14. Funding	14
15. Data availability	15
16. Ethics approval	16
17. Author contributions	17
18. Competing interests	18
19. Correspondence	19
20. Additional information	20
21. Supplementary material	21
22. References	22
23. Appendix	23
24. Bibliography	24
25. Index	25
26. Glossary	26
27. Acknowledgements	27
28. Declaration of interest	28
29. Funding	29
30. Data availability	30
31. Ethics approval	31
32. Author contributions	32
33. Competing interests	33
34. Correspondence	34
35. Additional information	35
36. Supplementary material	36
37. References	37
38. Appendix	38
39. Bibliography	39
40. Index	40
41. Glossary	41
42. Acknowledgements	42
43. Declaration of interest	43
44. Funding	44
45. Data availability	45
46. Ethics approval	46
47. Author contributions	47
48. Competing interests	48
49. Correspondence	49
50. Additional information	50
51. Supplementary material	51
52. References	52
53. Appendix	53
54. Bibliography	54
55. Index	55
56. Glossary	56
57. Acknowledgements	57
58. Declaration of interest	58
59. Funding	59
60. Data availability	60
61. Ethics approval	61
62. Author contributions	62
63. Competing interests	63
64. Correspondence	64
65. Additional information	65
66. Supplementary material	66
67. References	67
68. Appendix	68
69. Bibliography	69
70. Index	70
71. Glossary	71
72. Acknowledgements	72
73. Declaration of interest	73
74. Funding	74
75. Data availability	75
76. Ethics approval	76
77. Author contributions	77
78. Competing interests	78
79. Correspondence	79
80. Additional information	80
81. Supplementary material	81
82. References	82
83. Appendix	83
84. Bibliography	84
85. Index	85
86. Glossary	86
87. Acknowledgements	87
88. Declaration of interest	88
89. Funding	89
90. Data availability	90
91. Ethics approval	91
92. Author contributions	92
93. Competing interests	93
94. Correspondence	94
95. Additional information	95
96. Supplementary material	96
97. References	97
98. Appendix	98
99. Bibliography	99
100. Index	100

BASICITY OF AMINES

L. J. Sacks

March 10, 1959

I. Introduction

A base may be defined either as a proton acceptor or from a more general view as an electron pair donor [Lewis (1)]. A Lewis acid, accordingly, is an electron pair acceptor. Many reactions may therefore be classified as acid-base processes.

The amines offer several advantages in the study of basicity: (a) They offer a wide range of size and configuration; (b) they are soluble in both polar and non-polar solvents; and (c) many undergo reactions in the gas phase.

II. Measurement of Basicity

While the definition of a Lewis base as an electron pair donor offers a definite criterion for basicity, a method for evaluating this characteristic is less universally accepted. Measurements of pK_b in aqueous solution indicate (Table 1) that, in general, primary amines are stronger bases than ammonia, secondary amines are the strongest bases but tertiary amines weakest (2-4). One would expect, however, that the third replacement of hydrogen by an alkyl group should continue the monotonic increase in basicity. Further irregularities are found with more complicated amines (vide infra). Yet it would seem that some relationship between basicity and substituent groups must exist. The remarkable success of the Hammett and Taft equations (5): $\log k/k_0 = \rho^* \sigma^*$ or $\log k/k_0 = \rho \sigma$ in correlating data for thousands of organic reactions led to attempts at similar correlation of the basicity of amines. Hall found that a plot of pK_a for substituted ammonium ions vs. σ^* [σ^* values, the "polar substituent constants" determined by Taft, are additive properties of the various substituent groups (5)] gave essentially a linear relationship for tertiary amines and somewhat poorer correlations for primary and secondary amines (2). Brown and Okamoto (6) modified the Taft equation to account for charged species as well as neutral molecules. Edwards (7) correlated data for twelve highly diverse manifestations of basicity, including complex ion formation, displacements on carbon, substitution in cis-[Co(en)₂NO₂H₂O]⁺² and even quenching of fluorescence by means of the equation:

$$\log \frac{k}{k_0} = \alpha E_n + \beta H, \text{ where } k \text{ is the equilibrium or rate constant, } E_n$$

is a "nucleophilic constant" characteristic of the donor, H is the relative basicity of the donor toward protons and α and β are substrate constants. Other criteria for basicity include solubilization of silver oxide (8), dipole moments (9), catalytic activity (10-12) and equilibrium constants as estimated from spectrophotometric (10,13) or potentiometric (3) methods.

1. 1. 1950

The first part of the report is devoted to a description of the work done during the year. It is divided into two main sections: the first section deals with the work done in the laboratory, and the second section deals with the work done in the field.

The second part of the report is devoted to a description of the results of the work. It is divided into two main sections: the first section deals with the results of the work done in the laboratory, and the second section deals with the results of the work done in the field.

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The third part of the report is devoted to a description of the conclusions of the work. It is divided into two main sections: the first section deals with the conclusions of the work done in the laboratory, and the second section deals with the conclusions of the work done in the field.

III. The Fundamental Manifestation of Basicity

The fundamental manifestation of basicity is the energy released when an acid and base combine. Generally, this energy is reported as ΔH , and gives a quantitative measure of the stability of the bond [see e.g., (14)]. As pointed out by Brown (14) and others (3,4), the medium in which the reaction is carried out will have a decided effect on the heat of reaction because of interactions with reactants and/or products. Hall (2,3,15) and Pearson (4,10) discuss the effects of hydrogen bonding of primary and secondary amines and ammonia in protonic solvents. Apparent irregularities in the order of basicity from that expected from polar effects of substituents are explained on the basis of interactions of amine and adduct with solvent. Differences between predicted and experimental orders of basicity may also be explained in terms of various "strains" that the amine undergoes in forming the adduct (16).

IV. Solvation Effects

The solvation of an ammonium or substituted ammonium ion involves not only gross solvation of the charged ion but also specific interactions between the hydrogens and the solvent molecules. Pearson and Vogelsong (10) cite evidence that in hydration the latter effect amounts to ca. 8 kcal per mole per hydrogen. Altshuller (17) has estimated that for ammonium ion hydration the entropy decrease is ca. 7 e.u. above that for a monatomic ion of comparable size. This is attributed both to charge distribution over the four hydrogens and to hydrogen bonding with water molecules. Hall claims that the energy of hydration of free amine bases is small and essentially constant (3), a rather surprising conclusion, considering the diversity of hydrogen bonding possibilities.

Attempts to eliminate solvation effects by employing non-polar solvents are useless. As pointed out by Pearson (3), benzene can exert an appreciable interaction with ionic species. Even alkanes retain a dielectric constant of ca. 2 (3), hence can interact appreciably with ionic solutes, especially the proton. The attraction of the proton for non-positive molecules has been substantiated by quantum mechanical calculations (18). The differences between the various classes of amines are thus explained (3,10) in terms of the degree of solvation of the corresponding ammonium ions. This predicts an order of basicity: NH_3 RNH_2 R_2NH R_3N , and accounts for the low basicity of tertiary amines. Combined with polar effects, this explains amine basicity fairly well for many cases. However, solvation effects on the acid and adduct also change from solvent to solvent, but are neglected here. Obviously, the nature of the medium will also have a profound effect on the acidity of the acceptor. This effect is seen in the measurements by Hall in non-aqueous solvents (15).

V. Elimination of Solvation Effects

To eliminate the solvating effects in solution, Brown, et al., measured a wide variety of amines in the gas phase, using BMe_3 as reference acid (19-24). A summary of their results is presented in Table 2. To interpret these and related results, Brown proposes

The following is a summary of the results of the study conducted by the author, which was designed to determine the effect of the administration of the drug, X, on the blood pressure of patients with hypertension. The study was conducted over a period of six months, during which time the blood pressure of the patients was measured at regular intervals. The results of the study showed that the administration of the drug, X, resulted in a significant decrease in the blood pressure of the patients, and that this effect was maintained throughout the study period. The author concludes that the drug, X, is an effective agent for the treatment of hypertension, and that it should be considered as a first-line drug in the management of this condition.

1. Introduction

The purpose of this study was to determine the effect of the administration of the drug, X, on the blood pressure of patients with hypertension. The study was designed to evaluate the efficacy of the drug, X, in the treatment of hypertension, and to determine whether the drug, X, could be used as a first-line drug in the management of this condition. The study was conducted over a period of six months, during which time the blood pressure of the patients was measured at regular intervals. The results of the study showed that the administration of the drug, X, resulted in a significant decrease in the blood pressure of the patients, and that this effect was maintained throughout the study period. The author concludes that the drug, X, is an effective agent for the treatment of hypertension, and that it should be considered as a first-line drug in the management of this condition.

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2. Materials and Methods

The study was conducted over a period of six months, during which time the blood pressure of the patients was measured at regular intervals. The results of the study showed that the administration of the drug, X, resulted in a significant decrease in the blood pressure of the patients, and that this effect was maintained throughout the study period. The author concludes that the drug, X, is an effective agent for the treatment of hypertension, and that it should be considered as a first-line drug in the management of this condition. The study was designed to evaluate the efficacy of the drug, X, in the treatment of hypertension, and to determine whether the drug, X, could be used as a first-line drug in the management of this condition. The study was conducted over a period of six months, during which time the blood pressure of the patients was measured at regular intervals. The results of the study showed that the administration of the drug, X, resulted in a significant decrease in the blood pressure of the patients, and that this effect was maintained throughout the study period. The author concludes that the drug, X, is an effective agent for the treatment of hypertension, and that it should be considered as a first-line drug in the management of this condition.

three types of steric strain (16): (a) F-strain, associated with bulky groups at the faces of the acid and/or base; (b) B-strain, resulting from compression and bond-bending within the groups attached to an atom, accompanying the formation of a bond; and (c) I-strain, an increase in the internal strain of a cyclic structure resulting from a new bond causing a change in bond angles.

These strains rationalize most -- but not all -- of the gas phase data and are applicable to solution phase (4,14). However, Hall says (2) that for tertiary amines the plot of pK_b vs.

$\sum \sigma^*$ shows no deviations as would be expected if B-strain were operative. Independent evidence for steric strain is found in the NMR spectra of sterically hindered dihydrophenanthrenes (25).

Brown's measurements of ΔH cannot be compared with equilibrium values, which must have variable temperature coefficients and hence cannot possibly be considered as fundamental manifestations of basicity. Hence, while certain of the arguments proposed in favor of solution effects are quite reasonable, they cannot be evaluated by any of the data which Hall or Pearson and Vogelsong present.

Brown's use of ΔH as the measure of bond energy seems unfortunate. The actual energy is ΔE , and the difference, typically of the order of 800 cal per mole, is not a negligible quantity. This will be especially pertinent if heats in solution (14) and in the gas phase are to be compared. Also, as shown by Tamres (26), certain corrections must be made to Brown's gas phase values to correct an experimental error.

Table 1. pK_b for Some Simpler Amines¹

Amine	NH_3	$MeNH_2$	Me_2NH	Me_3N	$EtNH_2$	Et_2NH	Et_3N
pK_b	4.76	3.36	3.29	4.28	3.25	2.90	3.25
Amine	$n-BuNH_2$	$(n-Bu)_2NH$	$(n-Bu)_3N$	$n-C_6NH_2$			
pK_b	3.39	2.69	3.17	3.36			

1. Value for ammonia from Willard, H.H. and Furman, N.H., Elementary Quantitative Analysis, 3rd Ed., p. 122, Van Nostrand Co., (1940). Other values from reference 4.

* * * * *

Table 2. Amine-BMe₃ Compounds; Gas Phase Dissociation

Amine	ΔH , kcal mole	$K_D^{100^\circ}$	ΔS	Ref.
NH_3	13.75	4.6	39.9	20
CH_3NH_2	17.64	0.035	40.6	20
$(CH_3)_2NH$	19.26	0.0214	43.6	20
$(CH_3)_3N$	17.62	0.472	45.7	20
$(CH_3)_3N$	17.66	0.501	45.9	21
ethylenimine	17.59	0.0284	40.1	22
trimethylenimine	22.48	0.000322	44.3	22
pyrrolidine	20.43	0.00350	43.5	22
piperidine	19.65	0.0210	45.0	22
Et_2NH	16.31	1.22	44.1	22
$EtNH_2$	18.0	0.0705	43.0	24
Pyridine	17.02	0.303	-	19
2-Picoline	Too highly dissociated to measure			19
3-Picoline	17.93	0.135	-	19
4-Picoline	19.47	0.106	-	19
Et_3N	Too highly dissociated to measure			23
$n-C_3-NH_2$	18.14	0.0598	43.0	24
$n-C_4-NH_2$	18.41	0.0470	43.2	24
$n-C_5-NH_2$	18.71	0.0415	43.9	24
$n-C_6-NH_2$	18.53	0.0390	43.2	24

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AMPHOTERIC AMIDES OF THE TRANSITION METALS

D. K. Straub

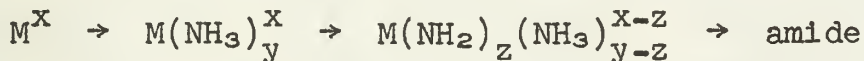
March 17, 1959

Introduction

The phenomenon of amphoterism probably occurs in all solvent systems, i.e. in both protonic and aprotic solvents. In the protonic solvent water, aluminum, zinc and chromium(III) form complex hydroxides. Sulfito complexes have been shown to form in the aprotic solvent sulfur dioxide (1). Schmitz-Dumont has been investigating the formation of complex amides in liquid ammonia. It is reasonable to assume that the formation of these complexes takes place in a stepwise fashion, even though few of the probable intermediates have been isolated. Deammonation of complex amides takes place in liquid ammonia much more readily than dehydration of complex hydroxides in water.

Transition metal amides

Preparation of the transition metal amides and complex amides entails the reaction of a soluble anhydrous salt of the metal with potassium amide in liquid ammonia. Probably a complex ammine is formed first upon solution of the metal salt in liquid ammonia; protons are then removed stepwise by the strong base, amide ion; deammonation may take place (depending on temperature) to give the compounds that are actually isolated:



amide \rightarrow mixed amide-imide \rightarrow imide \rightarrow mixed imide-nitride \rightarrow nitride

In many cases, spontaneous deammonation occurs, so that the intermediates have not been isolated. The amide compounds obtained from transition metal salts may be generally characterized as pyrophoric, polymeric, oxidizable, and easily hydrolyzable substances. The amides and complex amides are readily attacked by the acidic ammonium ion; the deammonated compounds are less readily attacked.

Titanium. Greenish-black titanium(III) amide reacts with excess potassium amide to form the green imide, $K[Ti(NH)_2]$ (2). The corresponding titanyl amide, $TiO(NH_2)_2$, is assumed to contain bridging oxo and amido groups, and reacts with excess amide to give the imide $TiO(NHK)_2$ (3). Upon heating, $(TiO)_3N_2$ and $(TiO)_3N_4K_8$ are formed from titanyl amide and imide, respectively. Both these nitrides are decomposed to titanium(II) oxide when strongly heated.

Zirconium. No simple amide of zirconium has been obtained. The rather complex ammonolysis product resulting from the action of ammonia on zirconium tetrabromide reacts with amide to form a yellow substance whose composition corresponds to $Zr(NK)_2 \cdot 2NH_3$ (4).

MEMORANDUM FOR THE DIRECTOR

DATE: 10/10/54

TO: DIRECTOR

Very confidential information has been received from a source who has been reliable in the past. This information concerns the activities of a group of individuals who are active in the field of [redacted] and who are active in the field of [redacted]. The source has provided information regarding the activities of this group and the individuals involved. The information is being provided for your information and for your use in the field of [redacted].

CONFIDENTIAL

Reference is made to the information received from the source regarding the activities of the group of individuals who are active in the field of [redacted] and who are active in the field of [redacted]. The information is being provided for your information and for your use in the field of [redacted].

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This information concerns the activities of a group of individuals who are active in the field of [redacted] and who are active in the field of [redacted].

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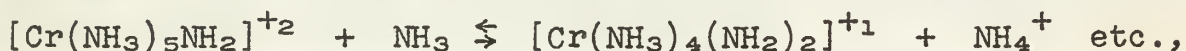
Vanadium. The black imide, $KV(NH)_2$ results from potassium amide and $K_3[V(SCN)_6]$ (5). Evidently deammonation of the hypothetical amide takes place so rapidly that only the imide can be isolated. This imide reacts slowly with ammonium ion in liquid ammonia; thus it is impossible to prepare the imide-amide, $HNVNH_2$, in accordance with the following equation:



Tantalum. Ammonolyzed tantalum pentabromide yields $Ta(NH_2)_4NHK$ and $Ta(NH_2)_3(NHK)_2$ with excess potassium amide (6).

Chromium. Light pink $Cr(NH_2)_3$ is obtained from potassium amide and $[Cr(NH_3)_6](NO_3)_3$ in liquid ammonia (7). With excess amide, $[Cr(NH_2)_4]nKn$ results. This splits off ammonia to give violet-black $[Cr(NH_2)_2]nKn$.

With chromium complexes in liquid ammonia, the ammonolysis reactions



lie far to the left (8). However, the equilibrium can be shifted by removal of the NH_4^+ with a strongly protophilic anion, like amide or an alcoholate. Thus $[Cr(NH_3)_6](OCH_2C_6H_5)_3$, prepared from the complex nitrate, potassium amide, and benzyl alcohol, reacts with ammonia to give bright gray-violet "amidochromium dibenzylate", $[H_2NCr(OCH_2C_6H_5)_2]$ (after drying in a stream of nitrogen). When freshly prepared, and before drying, this compound contains coordinated ammonia; it then will react with one mole of potassium amide to form violet $HNCr_2(NH_2)_3(OR)_2K$, and with five moles to form coffee brown $Cr(NH)_2K$. Amidochromium dibenzylate is assumed to possess bridging amido and benzylate groups. It also reacts with diphenylketene to give brown diphenylacetylchromium dibenzylate, $(OR)_2CrNHCOCH(C_6H_5)_2$, and with phenyl isocyanate to give what may be a biuret-like compound, containing one benzylate and two isocyanate groups per chromium. These polymers are reversibly depolymerized in pyridine solution.

If the benzylate anion is replaced by the phenolate anion, no ammonolysis takes place, due to the higher acidity of the phenol and consequent lower basicity of the anion (9). $H_2NCr(OC_6H_5)_2$ results when the phenylate is heated.

Molybdenum and tungsten. With excess amide, ammonolyzed molybdenum pentachloride and tungsten pentabromide give compounds having the composition $Mo(or W)(NK)_2NH_2$ (10). These have not yet been obtained pure.

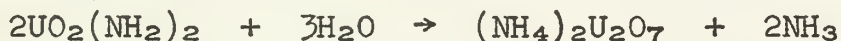
Manganese. Manganese(II) thiocyanate gives manganese(II) amide with potassium amide; this dissolves in excess amide, yielding light yellow $Mn(NHK)_2 \cdot 2NH_3$ (11).

Cobalt. At low temperatures, violet crystals of $\text{Co}_2(\text{NH}_2)_3(\text{NHK})_3$ can be isolated from the reaction between brown cobalt(III) amide (from hexamminecobalt(III) nitrate and potassium amide) and excess amide; at higher temperatures, the double nitride of potassium and cobalt, $\text{Co}_2\text{N}_3\text{K}_3$, is obtained (12, 13).

Nickel. Nickel (II) amide, a red crystalline substance, will dissolve in excess amide (14). From the resulting solution, red crystals of the composition $2\text{Ni}(\text{NH}_2)_2 \cdot 5\text{KNH}_2$ are obtained.

Thorium. When four moles of potassium amide are allowed to react with one mole of $\text{K}_2[\text{Th}(\text{NO}_3)_6]$ (chosen because it is an easily prepared, anhydrous, soluble salt of thorium) white $\text{HNTh}(\text{NH}_2)_2$ results, rather than the amide (15). At 50° , this product loses ammonia, forming $\text{Th}_2(\text{NH})_3(\text{NH}_2)_2$; at 100° , $\text{Th}(\text{NH})_2$, and at 130° , yellow Th_3N_4 , are formed. Colorless crystals of octamminethorium (IV) iodide, $[\text{Th}(\text{NH}_3)_8]\text{I}_4$, result from the reaction between thorium imide diamide and ammonium iodide. A variety of products are formed with excess amide: $(\text{HN})_2\text{ThNH}_2\text{K}$, $\text{HNTh}(\text{NH}_2)_3\text{K}$, and $\text{Th}(\text{NH})_3(\text{NH}_2)_4\text{K}_2$, depending upon the amount of excess potassium amide used. All of these are white and explode in air. These complexes decompose with rising temperature to $\text{Th}_2(\text{NH})_5\text{K}_2$, $\text{K}_3\text{Th}_3\text{N}_5$, and finally ThN .

Uranium. Uranyl amide, from potassium amide and $\text{K}[\text{UO}_2(\text{NO}_3)_3]$ is a brown substance which gives a diuranate, rather than the expected hydroxide, when hydrolyzed:



Its structure probably contains bridging amido groups. Uranyl amide reacts with ammonium iodide to form the diammine iodide, $\text{UO}_2(\text{NH}_3)_2\text{I}_2$, and with potassium amide to form the imide $\text{UO}_2(\text{NH})_2\text{K}_2$. Upon heating with ammonia in an autoclave, uranyl amide forms the imide UO_2NH , and finally uranium(IV) oxide. $(\text{UO}_2)_3\text{N}_4\text{K}_6$ results from heating $\text{UO}_2(\text{NH})_2\text{K}_2$.

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CONTENTS

1. The History of the United States	1
2. The History of the United States	2
3. The History of the United States	3
4. The History of the United States	4
5. The History of the United States	5
6. The History of the United States	6
7. The History of the United States	7
8. The History of the United States	8
9. The History of the United States	9
10. The History of the United States	10
11. The History of the United States	11
12. The History of the United States	12
13. The History of the United States	13
14. The History of the United States	14
15. The History of the United States	15
16. The History of the United States	16
17. The History of the United States	17
18. The History of the United States	18
19. The History of the United States	19
20. The History of the United States	20

PREPARATION AND PROPERTIES OF SILYLPHOSPHINE

Donald A. Wenz

March 24, 1959

I. Introduction.

Interest has been manifested recently in compounds containing phosphorus bonded directly to silicon. Emeleus and coworkers (1) have prepared a series of iodo-silyl-phosphines from white phosphorus with iodosilane. Iodosilane also reacts with trialkyl-phosphines to form the phosphonium type compounds $R_3P \cdot SiH_3I$.

Fritz observed that silane, on heating above 400° , gives hydrogen atoms and silyl radicals (2). This finding suggested that silane should react with ethylene, which was found to yield a number of products. It was therefore postulated that silane should undergo a similar reaction with other hydrogen compounds, including phosphine.

II. Preparation of silylphosphine.

Silylphosphine was prepared by passing a mixture of equal parts of silane and phosphine through a 60 cm. reaction zone at 500° (3,4). The effluent gases were condensed in traps cooled with liquid nitrogen. The hydrogen produced was pumped off, and the condensed products and reactants were separated by fractional distillation. A product was isolated that had a molecular weight of 64 and contained silicon and phosphorus in a ratio of 1:1, corresponding to the formula SiH_3PH_2 . Extrapolation of a linear plot of $\log p$ versus $1/T$ gave a value of 12.7° at 760 mm. for the boiling point of silylphosphine.

III. Reactions (4,5).

1. With hydrogen bromide.

If HBr is passed into a closed system containing SiH_3PH_2 at -80° , bromosilane and phosphine are formed. Phosphine was proved to be present by its reaction with mercuric chloride to form a yellow precipitate of $P(HgCl)_3$. Cleavage of the silicon-phosphorus bond by hydrogen bromide instead of formation of an addition compound may seem surprising, but Stock and Somieski (6) had observed analogous cleavage of the nitrogen-silicon bond in $(SiH_3)_3N$ by hydrogen chloride.

2. Hydrolysis.

a. Alkaline. Silylphosphine is not hydrolyzed readily by cold water. However, if dilute sodium hydroxide or ammonium hydroxide is added to condensed silylphosphine in the presence of methanol at liquid nitrogen temperatures and the mixture is then allowed to warm until it melts, hydrogen, phosphine, small amounts of silane, and silicic acid are formed. By observing the volumes of gases formed, it was found that three moles of hydrogen are produced per mole of silylphosphine, upon hydrolysis. Hydrogen arises from hydrolysis of the Si-H bonds after the molecule is cleaved.

b. Acid. In the presence of methanol at -50° , silylphosphine is hydrolyzed by dilute hydrochloric acid to give hydrogen, phosphine, small amounts of silane, and a solid silicon oxyhydride. Apparently the molecule is again split at the Si-P bond, and the postulated intermediate, H_3SiOH , is presumed to dehydrate to siloxane, which disproportionates to hydrogen and silicon oxyhydride (7). The latter compound may be of the type $(\text{SiH}_2\text{O})_x$. To substantiate this, chlorosilane was subjected to the same^x reaction conditions; the same silicon compounds were obtained.

3. Alcoholysis.

a. By ethanol and sodium ethoxide. Silylphosphine is not alcoholized by ethanol at -80° , but gas evolution is observed when ethanol and sodium ethoxide are used. Hydrogen and phosphine gases are evolved in the ratio 3:1, just as in the aqueous alkaline hydrolysis. Alcoholysis appears to proceed through cleavage of the molecule and subsequent reaction of the resulting ester with ethanol.

b. By ethanol and hydrogen chloride. When ethanol, saturated with hydrogen chloride gas, reacts with SiH_3PH_2 at -80° , there is slow evolution of phosphine; small amounts of hydrogen and silane are also formed. When gas evolution ceases and the solution is warmed to room temperature, a vigorous evolution of hydrogen, with traces of silane and phosphine, is observed. The reaction at -80° is believed to entail cleavage of the Si-P bond by ethanol, forming $\text{H}_3\text{SiOC}_2\text{H}_5$ and phosphine. The second reaction results in the decomposition of the ester into hydrogen, traces of silane, and a polysilicic acid ester that still contains silicon-hydrogen bonds.

4. Ammonolysis.

Silylphosphine is decomposed by liquid ammonia, with formation of phosphine, silane, and solid Si-N-H compounds as reaction products. The silicon-nitrogen-hydrogen compound is thought to be similar to the product obtained by Stock and Somieski (6), having a formula $(\text{SiH}_2\text{NH})_x$. This product is assumed to arise from cleavage of silylphosphine by ammonia to form phosphine and H_3SiNH_2 ; the latter then undergoes further decomposition.

5. Thermal decomposition.

On heating silylphosphine in a glass system in which the pressure can be measured, the variation in pressure with increasing temperature becomes non-linear at about 400° , indicating decomposition. The products were found to be hydrogen, silane, phosphine, and a high boiling, high molecular weight silicon-phosphorus compound. This compound undergoes reactions similar to those of silylphosphine itself.

6. With ethylene.

Since silane and silylphosphine undergo thermal decomposition by similar routes, it was expected that SiH_3PH_2 would also react with ethylene. Pressure measurements on a mixture of silylphosphine and ethylene at 430° indicated that such reaction does take place.

The products are difficultly volatile, oily liquids with strong reducing characteristics. Qualitatively, these products comprise silicon-organic compounds in which phosphorus is bonded directly to silicon.

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The following is a list of the names of the persons who have been appointed to the various committees of the Board of Directors of the American Telephone and Telegraph Company, for the year ending December 31, 1907.

COMMITTEES

1. Committee on Finance, consisting of Messrs. J. P. Morgan, Jr., Chairman, and Messrs. J. D. Rockefeller, Jr., and J. C. McLaughlin.
2. Committee on General Management, consisting of Messrs. J. P. Morgan, Jr., Chairman, and Messrs. J. D. Rockefeller, Jr., and J. C. McLaughlin.
3. Committee on Legal Affairs, consisting of Messrs. J. P. Morgan, Jr., Chairman, and Messrs. J. D. Rockefeller, Jr., and J. C. McLaughlin.
4. Committee on Engineering, consisting of Messrs. J. P. Morgan, Jr., Chairman, and Messrs. J. D. Rockefeller, Jr., and J. C. McLaughlin.
5. Committee on Sales and Distribution, consisting of Messrs. J. P. Morgan, Jr., Chairman, and Messrs. J. D. Rockefeller, Jr., and J. C. McLaughlin.
6. Committee on Construction, consisting of Messrs. J. P. Morgan, Jr., Chairman, and Messrs. J. D. Rockefeller, Jr., and J. C. McLaughlin.
7. Committee on Labor, consisting of Messrs. J. P. Morgan, Jr., Chairman, and Messrs. J. D. Rockefeller, Jr., and J. C. McLaughlin.

Some Inorganic Ring Systems

Richard L. Carlin

March 31, 1959

There are many inorganic compounds and groups whose structures are depicted as ring systems. Since a rather wide range of elements comprise such structures, there is a corresponding wide range in the properties and chemistries of these substances. Fundamental trends covering the following ring systems will be discussed: borazene, s-triazine, the phosphonitrilic halides, and tetrasulfur tetranitride.

I. Chemical Properties

A. Preparation

While the mechanisms of ring formation are quite obscure, there are several well-known synthetic methods whereby their synthesis can be accomplished. Borazene, $B_3H_3N_3H_3$, has been made by the pyrolysis of the ammoniates of the boron hydrides, and more recently by the reaction of a borohydride with ammonium ion (1) and by the reduction of $B_3Cl_3N_3H_3$ (2); derivatives are made by somewhat similar reactions (3-6). The more-recently discovered s-triazine, $(HCN)_3$, has been made by the acid-catalyzed polymerization of HCN (7,8) and by the reduction of the methylmercapto triazine (9). The trimeric phosphonitrilic halides, $(NPX_2)_3$, are best made by the reaction of the phosphorus pentahalide with the ammonium halide (10-13); the fluoride is made by treating the chloride with $KSCF$ (14). Tetrasulfur tetranitride, N_4S_4 , has been prepared by the reaction of sulfur with liquid ammonia; the preferred method entails interaction of ammonia with a sulfur chloride (11, 15-17).

B. Structure and Physical Properties

All these compounds and their derivatives, except N_4S_4 , are characterized as six-membered planar cyclic structures, with alternating Z-N atoms (18-23). Tetrameric $(NPCl_2)_4$ (24) and $S_4(NH)_4$ (25) represent puckered ring systems, while N_4S_4 consists of a bisphenoid of sulfur atoms intersected by a square with nitrogen atoms arranged along the edges (26). Several recent measurements have been made of physical properties (27-29); the infrared spectrum of each of the trimeric compounds shows a band characteristic of the particular ring system (19, 22, 30, 31).

C. Some Reactions

Reduction of borazene derivatives yields the corresponding hydro-derivatives (32); Grignard reagents have been used to convert, for example, $B_3Cl_3N_3Me_3$ to $B_3Et_3N_3Me_3$ (32,33). Substituted borazenes have also been prepared directly (34,35), as by the action of borohydride ion on anilinium chloride to produce $B_3H_3N_3(C_6H_5)_3$. A polycondensate of a borazene has recently been reported (35a), as has the nature of the pyrolysis product of the borazene-methanol adduct (35b). The $(CN)_3$ ring of $(HCN)_3$ is quite reactive, as it is cleaved by hydrazine (36), primary amines (37), amide ion, and by Friedel-Crafts Catalyst (38). Cyanuric chloride has been aminolyzed (39) and generally acts as an acid chloride; the fluoride is prepared by the action of

There are many reasons why it is not possible to have a perfect system of medicine. One of the main reasons is that the human body is a very complex system. It is made up of many different parts, each of which has its own function. These parts are all interconnected, and they all work together to keep the body healthy. This makes it very difficult to study the human body, and it is even more difficult to find a way to treat a disease. Another reason why it is not possible to have a perfect system of medicine is that the human mind is a very complex system. It is made up of many different parts, each of which has its own function. These parts are all interconnected, and they all work together to keep the mind healthy. This makes it very difficult to study the human mind, and it is even more difficult to find a way to treat a disease.

1. Chemical Properties

A. Physical Properties

The physical properties of a substance are those which can be observed without changing the substance. These properties include color, odor, taste, density, melting point, boiling point, and solubility. The chemical properties of a substance are those which can only be observed by changing the substance. These properties include reactivity, flammability, and toxicity. The physical properties of a substance are usually determined by simple experiments. The chemical properties of a substance are usually determined by more complex experiments. The physical properties of a substance are usually determined by simple experiments. The chemical properties of a substance are usually determined by more complex experiments.

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C. Biological Properties

The biological properties of a substance are those which can only be observed by changing the substance. These properties include reactivity, flammability, and toxicity. The physical properties of a substance are usually determined by simple experiments. The chemical properties of a substance are usually determined by more complex experiments. The physical properties of a substance are usually determined by simple experiments. The chemical properties of a substance are usually determined by more complex experiments.

SbF_3Cl_2 or KSO_2F on the chloride (40-42). The reaction of the chloride and fluoride with various nucleophiles has also been studied (42a).

The azide (43), hydrazide (44), and isothiocyanate (45) of the $(\text{PN})_3$ ring have recently been prepared from the chloride. Trimeric $(\text{NPCl}_2)_3$ undergoes Grignard and Friedel-Crafts reactions; the methyl (46) and phenyl (47) derivatives have also been made directly. Various alkylamino derivatives have been prepared, several of which have been shown to be isomeric (48-50). The behavior of the chloride and fluoride toward several basic reagents has recently been studied (50a). Tetrasulfur tetranitride is reduced to $\text{S}_4(\text{NH})_4$ by stannous chloride in ethanol; with acetyl chloride it yields $\text{S}_4\text{N}_3\text{Cl}$ (51). Fluorination yields $\text{S}_4\text{N}_4\text{F}_4$, while chlorination yields $\text{S}_3\text{N}_3\text{Cl}_3$ (15, 52). Transition metal derivatives of N_4S_4 have been made (53), as well as several alkyl derivatives (54, 55). A compound similar to $\text{S}_4(\text{NH})_4$ is heptasulfurimide, S_7NH (56, 57).

II. Aromaticity

In all these compounds the Z-N bond distances are individually equal, and the trimers are planar. This evidence, coupled with an extensive examination of their chemical properties, has been the basis from which a discussion of aromaticity in these systems began. Borazene is isosteric with benzene, and appears to resemble it remarkably in physical properties, while in the P-N and S-N rings there is a possibility of p-d π -bonding and consequent delocalization. This phenomenon has been explored, using the molecular orbital theory (58, 59).

III. Quadrupole Resonance

Cyanuric chloride (60-65) has been studied extensively through its quadrupole resonance frequency of absorption, as has $(\text{NPCl}_2)_3$ (66, 67) and $(\text{ClSN})_3$ (68). This work has demonstrated the double-bond character of the bond between chlorine and a ring atom, and has shown that all the chlorines in these molecules are not crystallographically equivalent.

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SEPARATION OF COORDINATION COMPLEXES BY ADSORPTION METHODS

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I. Introduction.

A problem of increasing importance in modern coordination chemistry entails the separation and analysis of reaction mixtures of robust complexes. Because classical and spectrophotometric methods can only be used in special cases, the problem is attacked from a different angle, by the adsorption methods.

Historically, the adaptation of adsorption to analytical and preparative procedures is credited to Dr. M. Tswett, a Russian botanist, who in a series of three articles published in 1906 (1), first called attention to the possibilities of this phenomenon and devised a method for its use. Except for a few sporadic applications, it lay buried in the literature for 25 years. Its utilization in 1931, by Kuhn and Lederer (2), for the resolution of complex organic mixtures awakened the scientific world to its almost unlimited possibilities. About five years later, Schwab and his co-workers (3) applied chromatography to inorganic separations.

E. Lederer and M. Lederer (4) distinguish between three types of chromatography; adsorption chromatography, ion exchange chromatography and partition chromatography. This distinction is however more or less arbitrary.

II. Adsorption Chromatography.

Although the columnar adsorption procedure appears to be simple and straightforward, its efficiency and its applicability are influenced by many interrelated factors.

Certain substances, such as alumina, magnesia, silica, carbon, starch and many others, both organic and inorganic, have the property of attracting to and retaining other substances on the surfaces of their particles. In a purely physical type of adsorption, where the attraction between the adsorbent and adsorbate is considered to be a function of the Van der Waals forces, the solute is usually easily eluted and is recovered in its original form. There exists another type, which is termed chemisorption, where upon elution or desorption, the solute is less easily eluted and may not be recovered in the form in which it was first adsorbed. Strain (5) explains the mechanism of chromatographic analysis as a dynamic process which depends on the repeated sorption, desorption and resorption of the solute to be separated.

A. The Column

The adsorption column can be of almost any size, shape, length, or design to suit the problems or whims of the analyst. Both pressure and vacuum may be used. Pressure is preferable since vacuum

tends to boil off the eluant and disrupt the column.

B. Adsorbents

No universal adsorbent has yet been found nor has a perfect adsorbent for any given purpose been developed. However, as a result of experience with many different solids, the more desirable characteristics of an adsorbent have now been developed.

The most satisfactory adsorbents are the alkaline earth oxides, hydroxides, and their salts, such as carbonates and sulfates. Alumina, carbon, ferric oxide and paper are also commonly used. Talc, silica, soda ash and various silicates have been found useful for special purposes. Advances have also been made in the utilization of organic adsorbents for the resolution of inorganic compounds.

C. Solvents and Eluants

There is no sharp demarcation between solvents and eluants. Liquids that serve for the adsorption of some compounds may be used for the elution of other substances with lower adsorbabilities. Choice of a solvent is determined to a large extent by the solubility of the materials to be adsorbed and by the activity and solubility of the adsorbent. Eluants, as a rule, are chosen with the object of obtaining rapid and complete liberation of adsorbed compounds. Some of the eluants, arranged in order of increasing polarity, that have found extensive use are, pentane, cyclohexane, benzene, chloroform, ether, acetone, alcohol, and acetic acid. Eluants of intermediate polarity may be obtained by using mixtures of solvents (6).

III. Separation of Cobalt(III) and Chromium(III) Ammines.

Jensen, Bjerrum and Woldbye (7) have reported the development of a useful method for analyzing aqueous mixtures of robust complexes. This method, a modification of the adsorption method, is called displacement analysis.

The separations were found to be highly dependent on the salt applied, being in some cases limited to special kinds of electrolytes. Thus $\text{Co}(\text{NH}_3)_6^{+++}$ could be separated quantitatively from $\text{Cr}(\text{NH}_3)_6^{+++}$ with 0.01 M KOH, 1 M KCl as a displacing agent with much better results than with basic solutions of NaCl or $\text{N}(\text{C}_2\text{H}_5)_4\text{Cl}$. On the other hand, alkaline $\text{N}(\text{C}_2\text{H}_5)_4\text{Cl}$ was necessary for separating mixtures of Coen_3^{+++} and Cren_3^{+++} .

For quantitative studies the collected samples of a given component are diluted to a known volume in a measuring flask and the absorption curve of the solution measured with a recording Cary spectrophotometer. The absorption curve of the initial solution of the pure component diluted to the same extent is measured with the same instrument. In this way information about the quality of the separations is obtained.

In the analysis of the mixture of cobalt(III) ammines (Hexammine, hydroxopentammine and dihydroxotetrammine) the hexammine and pentammine are first displaced leaving the tetrammine on the column; they are then separated on another column. In studying the decomposition of chromium(III) ammines, Jorgensen and Bjerrum (8) have used a

procedure for separating hexammine, hydroxopentammine, and dihydroxotetrammine which in principle is similar to that described for the corresponding cobalt(III) complexes.

The chromatographic method is also suitable for the separation of cis and trans complexes. An alkaline equilibrium mixture of the cis and trans dihydroxobis-ethylenediamine-cobalt(III) ions have been analyzed. The trans compound was first displaced by means of 0.1 M NaOH, 1 M NaCl, and the cis compound afterwards by means of the stronger displacing agent 0.1 M NaOH, 1 M LiCl. Woldbye (9) has determined the cis-trans equilibrium constant for the dihydroxobis-ethylenediamine-chromium(III) ions using a similar procedure.

The well known series of nitroammine complexes, $\text{Co}(\text{NH}_3)_6-x(\text{NO}_2)_x^{3-x}$, where $x=0, 1, 2, 3$ and 4, have been examined. The conditions under which they can be separated in cases where two or three of the complexes are present simultaneously, have been established.

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FERRIC PHOSPHATE COMPLEXES

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I. Introduction

It is well known that a solution of ferric salt becomes colorless on the addition of orthophosphoric acid. This reaction has been widely utilized in analytical chemistry. The decolorizing effect has been attributed to the formation of a colorless complex or of complexes of ferric iron with phosphoric acid by Weinland and Ensgraber (1). Carter and Clews (2) showed that phosphoric acid lowers the oxidation potential of $\text{Fe}^{++} - \text{Fe}^{+++}$ system. Bonner and Romeyn (3) observed that the reversible reaction $\text{Fe}^{++} + 1/2 \text{I}_2 (\text{aq.}) \rightleftharpoons \text{Fe}^{+++} + \text{I}^-$ goes to completion in the presence of phosphoric acid. All the complexes reported do exist, under different conditions. Ferric phosphate complexes are derived from the $[\text{Fe}(\text{H}_2\text{O})_6]^{+++}$ ion by the substitution of phosphate ions, and possibly of other anions present in the solution, for the water molecules in the complex. Van Wazer and Callis (4) has recently reviewed metal complexing by phosphates.

II. Physical Methods

There are many methods which can be applied to the investigation of complex formation (5).

A. Spectrophotometric Methods.

The spectrophotometric method is especially well suited to the study of complexes not sufficiently stable to permit their isolation from solution. Work of this type has been done by Job, who developed the Method of Continuous Variations, and extended by Vosburgh and Cooper (6), particularly to deal with the formation of more than one complex.

Lanford and Kiehl (7) determined the composition of the iron-phosphate complex by applying Job's method in ferric nitrate-phosphoric acid mixtures employing SCN^- solution for the colorimetric determination of ferric ion. According to the data, the composition corresponds to a 1:1 complex, i.e., $\text{Fe}(\text{HPO}_4)^+$. Its dissociation constant, 4.44×10^{-10} , has been evaluated at an ionic strength of 0.665 and 30° . These data cannot be considered reliable since the formation of different iron thiocyanate complexes was not taken into account.

Banerjee (8) used several different physico-chemical methods; the composition which he determined for the complex agreed with Lanford's result. But he detected, in addition to $\text{Fe}(\text{HPO}_4)^+$, another complex having the formula $\text{Fe}(\text{HPO}_4)_2^-$.

Pilipenko and Ivashchenko (9) studied the complexes by using a colorimetric method in the ultraviolet region, and found the complex with the ratio $\text{Fe}^{+++} : \text{PO}_4^{-3}$ of 2:1.

Ram, Bose and Kumar (10) concluded that the complexes are probably $[\text{FeCl}(\text{H}_2\text{PO}_4)_3]^-$ in the presence of chlorides and $[\text{FeSO}_4(\text{H}_2\text{PO}_4)_2]^-$ in the presence of sulfates. When monochromatic light passes through a transparent, colored medium, part of it is absorbed, part is reflected and the rest is transmitted. Transmission (T) is related to the concentration of coloring substance according to the equation: $T = \text{Re}^{-kcl}$, $kcl = D$. Optical density was calculated from the respective values of T using the above equation and was plotted against the molar concentration of phosphoric acid present in the different solutions.

B. Electrometric Methods.

Among the important quantitative data obtainable by polarographic means are dissociation constants of complexes, coordination numbers of metal ions, and the degree of stabilization of various oxidation states. Polarographic studies were carried out by using the supporting electrolytes because of the reduction of ferric ions by mercury by Ram, Bose and Kumar (11). It has been shown that one of the complexes formed in the system $\text{FePO}_4 - \text{H}_3\text{PO}_4 - \text{NaH}_2\text{PO}_4$ is $[\text{Fe}(\text{H}_2\text{PO}_4)_4]^-$ and the dissociation constant of the complex containing four $(\text{H}_2\text{PO}_4)^-$ groups is the order of 10^{-9} .

Dede (12) used a conductivity method for the determination of phosphate complexes in solution. A sharp increase in conductivity upon combination of H_3PO_4 and FeCl_3 was explained by the formation of a very strong acid $\text{H}_3[\text{FePO}_4\text{Cl}_3]$.

Ricca and Meduri (13) have obtained a maximum at a 1:1 mole ratio from conductometric measurement of $\text{FeCl}_3 - \text{H}_3\text{PO}_4$ mixtures, and have formulated the compound as $\text{H}_3[\text{FePO}_4\text{Cl}_3]$ in agreement with Dede's result.

Jensen (14) also discussed the decoloration of a solution of FeCl_3 with H_3PO_4 and disagreed with the conclusions of others. From the results of his own experiments entailing solubility and conductivity measurements, he concluded that the complex is a pure phosphate complex and not a mixed chlorophosphate complex.

Potentiometric titrations commonly used in determining the end point of precipitation and oxidation-reduction reactions are adapted for studying the complex-forming reactions.

Ram and his coworkers carried out titrations with solutions of different ferric ion concentrations. From the values of the e.m.f. (E) obtained for different volumes of the standard phosphoric acid added (V), values of dE/dV were calculated and plotted against corresponding values of V. From the amounts of H_3PO_4 added at these peaks, the corresponding ratios of $\text{H}_3\text{PO}_4/\text{Fe}$ were calculated.

Conductometric measurements of dilute solutions of FeCl_3 to which varying amounts of concentrated H_3PO_4 have been added suggest formation of 1:1 and 1:2 complexes which have been formulated as $[\text{Fe}(\text{HPO}_4)]^+$ and $[\text{Fe}(\text{HPO}_4)_2]^-$. Transport experiments indicate that cationic and anionic complexes are present since iron migrates to both cathode and anode.

C. Other Methods.

Banerjee also studied this problem by applying the thermometric titration method proposed by Halder (15). He obtained three breaks in the thermometric titration curve corresponding to $\text{FeCl}_3:\text{H}_3\text{PO}_4$ ratios of 1:1, 2:3 and 1:2. The break corresponding to the 2:3 ratio was considered to represent a mixture of 1:1 and 1:2 and this might not represent a new compound.

Salmon and coworker (16) studied the complexes by using ion exchange resins. They concluded that the complex ion contains at least three phosphate groups and can be represented by either of the formulas, $[\text{Fe}(\text{HPO}_4)_3]^{-3}$ or $[\text{Fe}(\text{PO}_4)_3]^{-6}$. Evidence for the presence of ions with a lesser number of phosphate groups was stated to be not very convincing.

III. Conclusion

A number of complex ions are formed but their nature has not been definitely established. The concept of the formation of soluble complexes--whether by strong ion association or covalent bonding--has been used to the present day for interpreting various chemical anomalies found in phosphate solutions. The higher values of pK_d obtained for the iron complexes may involve iron-oxygen bonds exhibiting appreciable covalent character.

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SOLID ROCKET PROPELLANTS

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I. INTRODUCTION

Progress in the science of rocketry during the past twenty years has been so rapid that laymen have had a difficult task in trying to keep up with developments. Even though, at the present, almost every so-called news publication abounds with references to rocketry it is doubtful whether sufficient basic knowledge of rocketry is generally available to appreciate and understand the new developments in the field.

II. BASIC PRINCIPLES OF ROCKETRY^{8,10}

Before proceeding to a discussion of solid propellants it may be helpful to present some basic information on rocketry.

The chief purpose of the rocket engine is to deliver thrust or force in a given direction for a given period of time. The thrust is obtained from the ejection of microscopic particles generated completely from substances carried within the system itself. This method of operation depends upon the physical laws of action and reaction and may be expressed by:

$$F = m a$$

in which the force or thrust F is equivalent to the product of a mass, m , and the acceleration of that mass, a . In a rocket the burning propellant gives gases or solids at high temperatures and pressures. The gases are accelerated from the engine ($m \times a$) to produce thrust.

The purpose of a rocket engine is to produce an impulse, i.e., the integral of thrust for a given period of time, t . When the thrust is constant the impulse, I is given by:

$$I = F t$$

A useful method of evaluating performance is the propellant specific impulse, I_{sp} , which is defined as:

$$I_{sp} = \frac{Ft}{W_p}$$

where W_p is the propellant weight. Specific impulse is usually expressed in seconds.

Further it may be shown that

$$V_{ex} \propto \sqrt{T_c / M}$$

where V_{ex} is the actual exhaust velocity, T_c , the combustion chamber temperature, and M , is the average molecular weight of the combustion products.

The relationships presented above serve to define two desirable properties for rocket propellants:⁵

- (1) Small negative or preferably positive heat of formation.
- (2) Low molecular weight and large negative heat of formation for the reaction products.

III. TYPES OF SOLID PROPELLANTS^{8,10}

A. Monopropellants (Single Base)--

A monopropellant is a single chemical compound which is stable at normal temperature and pressure but which is sufficiently reactive at elevated temperatures and pressures to convert the heat of decomposition of the compound into jet kinetic energy without reaction with external compounds. This type of propellant is represented by cellulose nitrate.

B. Homogeneous Propellants (Double Base)--

A homogeneous propellant is a propellant in which the oxidizing and reducing agents (or a mixture of monopropellant materials) occur as a single, or colloidal phase. An example of this type of propellant is cordite in which cellulose nitrate is colloided with another monopropellant such as glycerol trinitrate or DEGN.

C. Heterogeneous Propellants (Composite)

Such propellants are composed of a mixture of oxidant and reductant, each of which is present as a separate phase. Common black powder is an example of this type of propellant.

For many years homogeneous propellants were used almost exclusively; it is only quite recently that the more powerful composite propellants have come to the fore.

IV. APPLICATION OF SOLID PROPELLANTS^{8,9}

After a solid propellant is compounded it must be given a specific shape for use in a rocket. There are many possible shapes for solid propellant charges, each having its advantages and disadvantages. For maximum impulse it would be desirable to fill the entire rocket chamber with propellant and burn the propellant from the end, like a cigarette. This would be fine if a propellant composition could be found which would burn at a rate of 30 - 100 in./sec., however, current propellants burn at 2 in./sec. or less. In order to obtain burning times of the required duration, it is necessary to restrict the total burning distance. This means that burning must occur radially in a cylindrical charge rather than axially.

From a practical viewpoint the many different charge shapes may be divided into three classes, each characterized by the method by which it burns. They are: (1) internal - external burning charges, (2) external burning charges, and (3) internal burning charges. Each of these charge shapes possesses its own specific burning characteristics.

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LIQUID PROPELLANT ROCKETS

N. J. Rose

May 5, 1959

INTRODUCTION

The desire for bigger and better rockets has greatly stimulated a variety of research and development activities, including studies of the fundamentals of combustion,¹⁰ development of high energy fuels, and the development of refractory coatings for rocket engines.¹¹ Moreover, the rocket industry has had a profound effect in many non-scientific areas as is suggested by the following statement taken from a recent issue of C. and E. News:

The U. S., reacting from a swift kick in the scientific pants from Russia on October 4, 1957, grimly started out to make 1958 a year of catching up. More than national pride as the world's scientific leader was involved; at stake was survival itself.⁸

Thus, the political and strategic implications of the rocket "race" are currently subjects of great interest.² The economy of the nation has also felt the impact of the rocket industry. The national missile program consumes 20% of the nation's oxygen output,⁹ has greatly stimulated the perchlorate market,¹² and in general pours approximately 2,500 millions of dollars into the economy annually.⁷

In addition to international competition there is a good deal of rivalry within the rocket industry itself, concerning the relative merits of liquid and solid propellant units. According to John P. Longwell, Esso Research and Engineering, liquid propellants will always give a slightly more favorable performance (I_{sp}) but the reliability of solid fuels will make them more desirable for military purposes.¹⁵

Liquid propellants may be classified as monopropellants or bipropellants. A monopropellant does not require the addition of another ingredient to bring about the release of its thermochemical energy. The bipropellant has two compounds and may be either hypergolic (self-igniting) or nonhypergolic.³ A consideration of the desirable properties of liquid propellants provides a convenient format for their discussion.

DESIRABLE PROPERTIES

A. Propellants should have small negative or preferably positive standard heats of formation and should form reaction products with large negative heats of formation and with low molecular weight.^{1,3,7} The performance of a propellant system is measured as specific thrust, I_{sp} , which is the thrust per unit weight rate of flow of the propellant. The specific thrust is a function of the square root of the term T_c/M where T_c is the combustion temperature and M is the average molecular weight of combustion products.^{13,14}

High heats of formation would tend to give a high T_c and low molecular weight products would make the T_c/M ratio large. Both of these criteria are satisfied when the propellants of a system are either the elements of the first rows of the periodic chart or compounds composed of these elements. Table I contains some representative performance values for particular propellants.

TABLE I⁵

<u>Oxidant</u>	<u>Fuel</u>	<u>Mixture Ratio O/F</u>	<u>Specific Thrust lb./lb./sec.</u>
Liquid oxygen	liquid hydrogen	3.4	360
Liquid oxygen	ethanol 100%	1.5	240
RFNA	aniline	3.0	

Attaining maximum thrust necessitates optimum combustion conditions. This means that a smooth feeding system and efficient injection system are required.

1. Feed Systems

a. Simple pressure feed systems utilize the pressure from the boiling oxidant (e.g., liquid oxygen), from a high pressure third tank, from a small solid propellant cartridge, or from spontaneous ignition of part of the main fuels to drive the fuel into the combustion chamber.^{3,4}

b. The turbo-pump system uses the gases from a small generator to drive a turbine which in turn drives the fuel pumps. The gas generator may use solid propellants, a liquid propellant different from that used in the main rocket, or it may use one of the components of the main propellants (e.g., the gas obtained by passing H_2O_2 from main oxidizer tank over a surface catalyst).

2. Injectors

a. A shower head injector provides a fine spray and therefore rapid evaporation rates. It is useful for nonhypergolic propellants where the combustion rate is probably controlled by a gas-phase chemical reaction. Mixing of the liquids would have little effect on the combustion rate.^{1,3,6}

b. A liquid-liquid impinger is commonly used for hypergolic bipropellant systems because any operation which facilitates liquid-liquid collisions and liquid-phase chemical reaction rates will allow maximum combustion rates.¹

c. Splash plates are often used when the reaction is surface catalyzed.¹

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TABLE I

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Great care is taken to design the feeding and injection systems so that high-frequency pressure oscillations do not develop during combustion.³ Frequently these oscillations can become severe enough to destroy the rocket.

B. Propellants should have high densities so that dead weight of storage tanks and the increased size of the rocket as a whole may then be avoided.¹

C. At least one of the propellant components should have a relatively high boiling point and high specific heat.¹ The high temperature produced by the operation of a rocket requires that the chamber walls be protected in some way. Several cooling systems have been successfully used.^{4,5}

1. Concentric feed. In this system, the fuel is injected so that it forms a concentric cylinder around the injected oxidant and therefore protects the chamber wall to some extent.

2. Regenerative cooling. One of the propellant components flows through the annular passage between the chamber and the rocket wall before it is introduced into the chamber. In addition to cooling the chamber wall, this process increases the efficiency of the motor by reducing heat loss. This system can be modified simply by coiling the fuel lines around the chamber and nozzle.

3. Film cooling. Here, a portion of the fuel is injected through a series of orifices into the chamber to form a cooling film on the inner surface.

D. Propellants should be non-toxic, should not decompose or change chemically during storage, and should be readily available and relatively cheap. Only the last of these considerations requires comment. The price of liquid fluorine would drop from 5.00 dollars to 1.00 dollar per pound if there were a demand for daily multiton shipments.⁷

SUMMARY

The ignition and thrust of a rocket are related by a series of empirical correlations for which there is no satisfactory theoretical model. Thus, we see that the primary performance characteristic, the specific thrust, depends not only upon the chemical and thermodynamic properties of the propellant but also on the design of the various functioning units. These empirical relationships have provided a satisfactory basis for the development of successful rockets.

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INFRARED SPECTRA OF CHELATED CARBONYL COMPOUNDS

R. E. Sievers

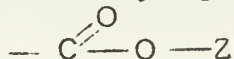
May 12, 1959

During the past decade infrared spectroscopy has become one of the most important tools in the hands of the coordination chemist. Organic ligands quite often contain functional groups which absorb light in the infrared region. Chelation of such ligands produces marked changes in frequency and intensity of certain absorption bands. It is sometimes possible to relate these changes to some characteristic of the resulting metal chelates. Of particular interest are the studies made on chelates of ethylenediaminetetra-acetic acid and on acetylacetone and its derivatives.

I. Chelates of Ethylenediaminetetra-acetic Acid (EDTA)

EDTA contains two nitrogen and four oxygen donor atoms, making it potentially a sexidentate ligand. Stable complexes are formed however in which one or more of the six donor atoms are not attached to the metal ion. The presence of an uncomplexed carboxyl group may be detected in the infrared spectra. Busch and Bailar¹ prepared cobalt complexes containing EDTA which in one case was sexidentate and in two other cases was pentadentate. The infrared spectra of the complexes containing pentadentate EDTA show two carbonyl bands. One band, at 1723 cm^{-1} is attributed to a free carboxyl group. A stronger band, appearing at 1628 cm^{-1} , is attributed to the presence of three coordinated carboxyl groups. In a compound containing a sexidentate EDTA group, only one absorption band is observed at 1628 cm^{-1} . This indicates that all four carboxyl groups are equivalent and coordinated.

Shifts to lower frequencies upon complex formation have been explained in terms of the partial ionic character of the coordinate link¹⁻⁷. If a carboxyl group is linked to some group Z



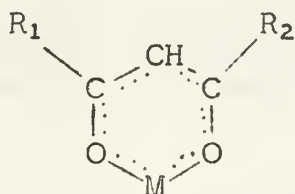
the carboxylate resonance will increase as the ionic character of the O-Z link increases². This results in a greater localization of electrons in the carbonyl group, imparting single bond character to the group and thus lowering the frequency.

An infrared study of Nd and Y complexes of EDTA led to the conclusion that the EDTA group is pentadentate and that a water molecule occupies the sixth coordination position³. Differential thermal analysis further supported this conclusion. Kirschner⁴ used infrared spectra as evidence for a coordination number of six for the Cu(II) complex of EDTA. Tetradentate and bidentate complexes of EDTA with Pd(II) and Pt(II) have also been studied⁵.

Sawyer and Paulsen⁶ have attempted to correlate stability of alkaline earth chelates with shifts in frequency. They also observed that the bonding in these complexes is primarily ionic. This was similarly found to be the case for complexes of Mn(II), Co(II), Ni(II), Zn(II), Cd(II), Hg(II), and Pb(II)⁷.

II. Chelates of β -diketones

A cyclic, symmetrical, resonance-stabilized structure is now generally accepted for metal acetylacetonates⁸.



The infrared spectra of these compounds is very rich in the region 1700 to 280 cm^{-1} and assignment of the absorption bands is difficult. In the sodium chloride region, bands arising from $\text{C}=\text{O}$ and $\text{C}=\text{C}$ stretching modes are of prime interest.⁹ In the cesium bromide region, bands attributed to $\text{M}=\text{O}$ stretching have been reported.¹⁰

Infrared spectra of chelates of acetylacetone with beryllium, magnesium, chromium, iron, cobalt, copper, zinc, thorium, uranium, nickel, aluminum, scandium, americium, samarium, boron, titanium, zirconium, cesium, potassium, sodium, lithium, thallium, silver, calcium, palladium, and lanthanum have been studied.⁸⁻¹⁴

The effect of varying groups R_1 and R_2 has been studied in Cu and Ni chelates of derivatives of acetylacetone.⁹⁻¹³

The intense activity in this area may be attributed to attempts to relate the stability of these complexes to observed frequency shifts.

Bellamy and Branch¹² found a straight line relationship when they plotted the carbonyl frequencies versus the stabilities of bivalent metal complexes of salicylaldehyde. They reasoned that it should therefore be possible to utilize infrared measurements to determine stabilities. However when the spectra of copper chelates of various β -diketones^{12,13} were compared to their stability, no regular relationship was found.

Holtzclaw and Collman¹³ examined the spectra of acetylacetone chelates of several divalent metals and found a qualitative relationship between the strength of the $\text{M}=\text{O}$ bond and the frequency of the perturbed carbonyl absorptions. The frequency decreases as the stability increases for the series: Mg(II), Cd(II), Mn(II), Co(II), Zn(II), Ni(II), Cu(II). The nickel complex is the only exception. It absorbs at a higher frequency than this relationship would predict.

West and Riley¹⁴ studied acetylacetonates of univalent, divalent, and trivalent metals and attempted to relate the carbonyl band frequency to respectively the first, second, and third ionization potentials. They were successful for divalent and trivalent metals, but the relationship broke down for the univalent case.

Most recently¹⁰ interest has been shifted to the M—O frequencies in the potassium bromide and cesium bromide regions. Assignment of bands in these regions is very uncertain but preliminary work indicates that some correlation of complex stabilities to M—O stretching frequencies may be possible. Bands ranging from 420 to 480 cm^{-1} have been attributed to metal-oxygen stretching modes.

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CONTENTS

THE UNIVERSITY OF CHICAGO	1
LIBRARY	2
540 EAST 57TH STREET	3
CHICAGO, ILL. 60637	4
TEL. 773-9365	5
THE UNIVERSITY OF CHICAGO	6
LIBRARY	7
540 EAST 57TH STREET	8
CHICAGO, ILL. 60637	9
TEL. 773-9365	10
THE UNIVERSITY OF CHICAGO	11
LIBRARY	12
540 EAST 57TH STREET	13
CHICAGO, ILL. 60637	14
TEL. 773-9365	15
THE UNIVERSITY OF CHICAGO	16
LIBRARY	17
540 EAST 57TH STREET	18
CHICAGO, ILL. 60637	19
TEL. 773-9365	20
THE UNIVERSITY OF CHICAGO	21
LIBRARY	22
540 EAST 57TH STREET	23
CHICAGO, ILL. 60637	24
TEL. 773-9365	25
THE UNIVERSITY OF CHICAGO	26
LIBRARY	27
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CHICAGO, ILL. 60637	29
TEL. 773-9365	30
THE UNIVERSITY OF CHICAGO	31
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CHICAGO, ILL. 60637	34
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THE UNIVERSITY OF CHICAGO	36
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CHICAGO, ILL. 60637	39
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THE UNIVERSITY OF CHICAGO	41
LIBRARY	42
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CHICAGO, ILL. 60637	44
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THE UNIVERSITY OF CHICAGO	46
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CHICAGO, ILL. 60637	49
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THE UNIVERSITY OF CHICAGO	51
LIBRARY	52
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CHICAGO, ILL. 60637	54
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CHICAGO, ILL. 60637	64
TEL. 773-9365	65
THE UNIVERSITY OF CHICAGO	66
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